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IN MEMORY OF PROFESSOR N. A. VALYASHKO

(1871-1955)

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On January 25, 1955 in his 84th year, after a long illness, died one of the oldest Soviet chemists, Doctor of Chemical Science, Doctor of Pharmaceutical Science, Professor Nikolai Avksentevich Valyashko.

N. A. Valyashko was born in the town of Kupyansk (Kharkov region) on March 20, 1871 into the family of a pharmacist. For many years N. A. Valyashko worked as a pupil in Kharkov pharmacies, and later as a pharmaceutical assistant. His unusual thirst for knowledge and his persistence enabled him to pass the examination as a pharmacist, and in September 1895 he became an assistant in the pharmaceutical laboratory of Kharkov University. In the course of the subsequent 60 years N. A. devoted himself entirely to the training of chemists, pharmacists, engineers and young scientists, and to the development of organic and pharmaceutical chemistry in Russia. In 1896 he organized the teaching of analytical chemistry for pharmacists and established the new pharmaceutical laboratory at Kharkov University. In 1919 N. A. was chosen as professor of pharmacy and pharmacognosy. From 1919, after defending his dissertation for the degree of Doctor of Chemistry, up to the end of his life, N. A. occupied the chair of organic chemistry at Kharkov Institute of Technology, now the Kharkov V. I. Lenin Polytechnic Institute.

The scientific activity of N. A. was associated mainly with the study of two problems -- the chemistry of substances of medicinal importance and the structure of molecules as revealed by ultraviolet absorption spectra.

The phytochemical studies of N. A. had great practical importance. They enabled the raw material basis for the production of medicinal substances to be widened in the Ukraine. He made a chemical study of adonidine, rutin, robinine and campherol, components of fruits of prickly buckthorn, essential oils of Ukrainian plants, castor oil from the Ukrainian castor oil plant, etc. With E. I. Valyashko he developed a method of production of the casein preparation "calcaz" (calcium caseinate) for treatment of children's intestinal ailments. He prepared alkyl and acetyl derivatives of campherol (1,3,4,-trihydroxyflavanol); contrary to the view held at that time, he showed that the Kostanecki-Drager rule of the inability of hydroxyls in the vicinity of a carbonyl group to give methyl ethers is valid only for methylation with alkyl iodides. Thus, by the action of dimethyl sulfate on quercetin, he readily obtained trimethyl ethers.

The principal researches of N. A. were associated with ultraviolet absorption spectra. He was one of the pioneers of the extensive use of these spectra in the study of the structure of molecules and their behavior in presence of various solventsand reactants. Starting from 1908, at the very start of the development of the technique of measurement of these spectra, N. A. appreciated their enormous value not only for the study of chemical structure but also for the identification and analysis of complex mixtures of various substances. In 1910 he established the first Russian spectrographic laboratory. His school of spectrographic specialists was considered one of the best in the world both in its thoroughness and in the systematic character of the investigations of the ultraviolet absorption spectra of various chemical compounds. Actually, in respect of these characteristics, which are essential for any scientific investigation, his school differed markedly from those of Henri, Baly, Hantzsch, as well as from the contemporary schools, for example those of Ramart-Lucas or Morton.

N. A. and his pupils (Boltina, Druzhin, Bliznyukov, Shcherbakov, Lutsky, Voroshin, Depeshko, Lavrushin, Rozum, Cheshko, N. N. Valyashko, Ramazanovich, and others) studied, with the thoroughness typical of the work of N. A., the spectra of about 200 different mono-, di- and trisubstituted benzenes, pyrazoles, pyrazolones, etc., and all the determinations of the spectra were carried out as a rule in diverse solvents and in presence of various reagents. N. A. was indeed the first to widely apply various types of molecular interactions during examination of spectra with the objective of studying the fine structure of molecules. In their detail and accuracy, these investigations of spectra are a model of classical investigations; the data alone that were obtained were of enormous value; they were included, and continue to be included, in reference publications.

Analysis of the accumulated data enabled N. A. to establish the now generally known regularities of the absorption spectra of aromatic and heterocyclic compounds. He showed that the absorption curves of many complex molecules can be regarded as being made up of the superposed curves of simpler components of the molecules. He examined the problem of the nature of the influence of the formation of a hydrogen bond inside a molecule upon the position of the absorption band maxima. From the extent of the displacement of the maxima of the bands was calculated the energy of the hydrogen bond; the value so obtained agreed with that calculated by other methods.

Utilizing the established regularities, N. A. arrived at a number of interesting conclusions about the fine structure of molecules of various compounds. He established that a methylene group between two benzene rings is by no means (as generally assumed) isolated; he spectrographically proved the absence of hypothetical inner salts in o- and p-amino- and dimethylamino-substituted benzene sulfonic and benzoic acids; he also showed that a betaine structure was absent from their esters. Tautomerism was studied by N. A. in a number of investigations. He determined spectrographically the existence and character of tautomerism in resorcinol, phenylhydrazine, acetanilide, etc. Spectrographic study of salt formation in polyhydroxy compounds led to the conclusion that the different hydroxyls were not equivalent in value.

Particularly close attention was paid by N. A. to the spectrographic study of the relation between the structure of molecules and their physiological action. As a pioneer in this field, he put forward many interesting ideas and suggestions which await further confirmation and development. Also of interest are general concepts of the character of ultraviolet absorption spectra that were developed by N. A. He regarded the spectra of mono- and polysubstituted benzenes as the result of intensification and displacement of bands characteristic of unsubstituted benzene. The character of the spectrum of a substituted benzene, according to N. A., is determined mainly by the "distribution of unsaturated centers" in the benzene ring itself, while ". . . the nature of the atoms in part entering into the molecule in the form of substituted groups and even sometimes entering the nucleus of the molecule plays a secondary part". The benzene ring itself is, in his view, a dynamic system. Interaction between ring and substituents creates a new dynamic system derived from benzene, as the main center of movement, and differing in the development of one type of oscillations or another which determine the state of the molecule. These views of N. A. were also a solid contribution to the further development of the ideas of A. M. Butlerov and V. V. Markovnikov on the reciprocal influence of functional groups in a molecule, of A. M. Butlerov's conception of the chemical compound not as something dead and immobile but as a constantly moving system of the smallest particles.

N. A. constantly took a very active part also in the organization of the development of industry and science in our country. In 1924 he was a member of a committee of the People's Commissariat of Public Health for the publication of a National Pharmacopeia and a member of the Pharmacopeial Committee in Moscow. In 1926 he became a member of the Academic Medical Council of the People's Commissariat of Public Health of the Ukrainian SSR. From 1925 to 1938 N. A. was national editor of the Ukrainian Chemical Journal; in 1932 he bacame a member of the Presidium of the Chemical Development Committee under the State Planning Commission of the USSR.

In 1898 N. A. was admitted to the roll of members of the Russian Physico-chemical Society. He took an active part in it as secretary, later as Assistant Chairman and Chairman of the Kharkov section. After the Physico-chemical Society had been reorganized as the D. I. Mendeleev All-Union Chemical Society he became permanent chairman of its Kharkov section and member of the presidium of the organizing bureau of the society. He was president of the organizing committee at the convocation of the 6th Mendeleev Congress. In 1941 N. A. was chosen as honorary member of the society.

For his fruitful activity N. A. was honored by the Soviet Government with the Orders of Lenin and of Worker of the Red Flag; he was also awarded the medal "For valiant service in the Great Patriotic War of 1941-1945". The Ukrainian Government awarded him the title of honorary worker in science.

To all who knew him, N. A. will serve as an example of a man of self-sacrificing work, a patriot of our country, a man who gave his whole life to the service of Soviet science and the Soviet people.

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78. "Absorption Spectra and Structure of Benzene Derivatives, XIX. 2,5-Dihydroxyacetophenone and Its Methyl Ethers," J. Gen. Chem., 26, 294 (1956) (T.p.311) * (with N. N. Valyashko).

B. Papers prepared for publication

1. Absorption Spectra and Structure of Benzene Derivatives, XX. Spectrographic Investigation of p-Aminobenzenesulfonic Acid and Its Derivatives (with N. N. Romazanovich).

2. Absorption Spectra and Structure of Benzene Derivatives, XXI. p-Dimethylaminobenzenesulfonic Acid and Its Methyl Ester (with N. N. Romazanovich).

3. Absorption Spectra and Structure of Benzene Derivatives, XXII. Spectrographic Investigation of o- and m-Aminobenzene Sulfonic Acids and Their Derivatives (with N. N. Romazonovich).

* T. p. = C. B. Translation pagination

ABSORPTION SPECTRA AND STRUCTURE OF BENZENE DERIVATIVES

XIX. 2,5-Dihydroxyacetophenone and Its Methyl Ethers

N. A. Valyashko * and N. N. Valyashko

Syntheses. 2,5-Dihydroxyacetophenone was synthesized by the method of Nencki and Schmid [1]. Its methylation [2] gave 2-hydroxy-5-methoxy- and 2,5-dimethoxyacetophenone. 2-Methoxy-5-hydroxyacetophenone was prepared by the method of [3]. The prepared compounds were purified by recrystallization from appropriate solvents; 2,5-dimethoxyacetophenone was purified by two redistillations at 158° (14 mm).

Spectrographic Investigation

2,5-Dihydroxyacetophenone. The absorption of 2,5-dihydroxyacetophenone in ethanol at concentrations of $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M resembles the absorption spectrum of 2-hydroxyacetophenone; owing, however, to the conjugation of the 5-hydroxy group with the benzene ring and the carbonyl group, the band α_2 is more strongly developed (maximum at λ 3700 A and ε 9000) with a 1.8 times increase in intensity and displacement of the maximum by 450 A toward the long-wave region in comparison with band α_2 of 2-hydroxyacetophenone (Fig. 1, Curves 1 and 2).

Fig. 1. 1) 2,5-Dihydroxyacetophenone in ethanol $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M; 2) 2-hydroxyacetophenone in ethanol $10^{-2} - 10^{-4}$ M; 3) 3-hydroxyacetophenone in ethanol $10^{-2} - 2 \cdot 10^{-5}$ M.

* Deceased

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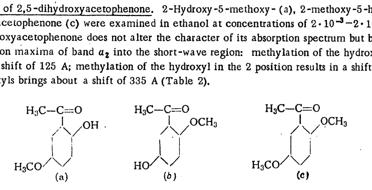
Furthermore the conjugation of the 5-hydroxy group with the benzene ring and the carbonyl group is reflected in the presence of a band a'_1 with a maximum at λ 2300 A and ϵ 32000, corresponding to band a'_1 in the spectrum of 3-hydroxyacetophenone but stronger (1.6 times) and displaced by 120 A in the direction of long waves; it is also superposed on band a_1 of 2,5-dihydroxyacetophenone with a maximum at λ 2500 A and ϵ 11000, intercepting a portion of the absorption (Fig. 1, Curves 1 and 3) in the extreme ultraviolet. Band a_1 of 2,5-dihydroxyacetophenone has nearly the same intensity as band a_1 of 2-hydroxyacetophenone and is situated 40 A farther toward the long-wave region.

The absorption spectra of 2,5-dihydroxyacetophenone are unaffected by solvents: in water, ethanol, dichloroethane and dioxane at the same concentrations, only slight shifts in the position of the bands and only slight changes in intensity are observed (Table 1).

TABLE 1

Solvents for 2,5-dihydroxyacetophenone ($2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M)	a_2 band		a_1 band		a'_1 band	
	λ	ϵ	λ	ϵ	λ	ϵ
Ethanol	3700	9000	2570	11000	2300	30000
Water	3550	6000	2565	10000	2320	20000
Dichloroethane	3525	8000	2550	18000	2285	35000
Dioxane	3590	6400	2540	11000	2290	30000

Methyl ethers of 2,5-dihydroxyacetophenone. 2-Hydroxy-5-methoxy- (a), 2-methoxy-5-hydroxy- (b), and 2,5-dimethoxyacetophenone (c) were examined in ethanol at concentrations of $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M. Methylation of 2,5-dihydroxyacetophenone does not alter the character of its absorption spectrum but brings about a shift of the absorption maxima of band a_2 into the short-wave region: methylation of the hydroxyl in the 5 position results in a shift of 125 A; methylation of the hydroxyl in the 2 position results in a shift of 300 A; methylation of both hydroxyls brings about a shift of 335 A (Table 2).



(a) (b) (c)

Such a large displacement of the band a_2 toward short waves in the case of 2-methoxy-5-hydroxy- and 2,5-dimethoxyacetophenones is caused by the rupture of the hydrogen bond between the hydroxyls in the 2 position and the oxygen of the carbonyl group, as had been demonstrated by N. A. Valyashko and Yu. S. Rozum [4] in the case of 2-methoxyacetophenone.

TABLE 2

Compounds (in ethanol solution)	a_2 band		a_1 band		a'_1 band	
	λ	ϵ	λ	ϵ	λ	ϵ
2,5-Dihydroxyacetophenone	3700	9000	2570	11000	2300	30000
2-Hydroxy-5-methoxyacetophenone . .	3575	6000	2555	9000	2275	40000
2-Meth~~oxy-5-hyd~~roxyacetophenone . .	3400	7000	2500	10000	2300	16000
2,5-Dimethoxyacetophenone	3365	9000	2505	12500	2245	25000

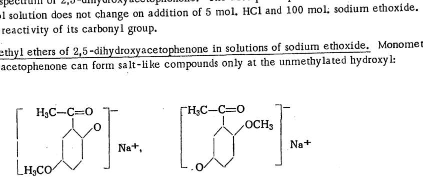
Solvents (water, ethanol, dichloroethane and hexane) have little influence upon the absorption spectra of the ethers. Only a small displacement of the maxima of the a_2 bands of 2-methoxy-5-hydroxyacetophenone in dichloroethane of 180 A and of 2,5-dimethoxyacetophenone in hexane of 125 A toward the shorter waves (concentration of $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M) is observed.

TABLE 3

Compounds	Solvent	a_2 band		a_1 band		a'_1 band	
		λ	ϵ	λ	ϵ	λ	ϵ
2-Hydroxy-5-methoxyacetophenone	Water	3610	5000	2540	10000	2250	45000
Ditto	Hexane	3600	5000	2565	8000	2265	45000
2-Methoxy-5-hydroxyacetophenone	Water	3340	7000	2510	11000	2270	16000
				Indication of an inflection			
2-Methoxy-5-hydroxyacetophenone	Dichloroethane	3260	4500	2450	20000	—	—
2,5-Dimethoxyacetophenone	Water	3340	5000	2540	8000	2300	20000
Ditto	Dichloroethane	3370	5000	2475	9000	2235	20000
Ditto	Hexane	3215	10000	2430	16000	2230	50000

Consequently the examination of the absorption spectra of 2,5-dihydroxyacetophenone and its methyl ethers in neutral solvents shows that neither methylation nor the action of solvents substantially alters the character of the absorption spectrum of 2,5-dihydroxyacetophenone. The absorption spectrum of 2,5-dimethoxyacetophenone in ethanol solution does not change on addition of 5 mol. HCl and 100 mol. sodium ethoxide. This indicates the poor reactivity of its carbonyl group.

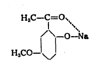
Isomeric monomethyl ethers of 2,5-dihydroxyacetophenone in solutions of sodium ethoxide. Monomethyl ethers of 2,5-dihydroxyacetophenone can form salt-like compounds only at the unmethylated hydroxyl:



This enables us to study spectrographically the properties of each hydroxyl separately.

2-Hydroxy-5-methoxyacetophenone was investigated in ethanol at concentrations of $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M in presence of 1, 10 and 100 mol. sodium ethoxide. Addition of only 1 mol. sodium ethoxide in ethanol at a concentration of $2 \cdot 10^{-3}$ M leads to formation of a sodium salt, and the edge of the absorption band is shifted to the extent of 450-500 A toward the long waves; dilution with ethanol leads, however, to complete alcoholysis of the salt (Fig. 2, Curve 3). Addition of 10 mol. sodium ethoxide results in suppression of alcoholysis on dilution, but the a_2 band does not develop fully, and only in presence of 100 mol. sodium ethoxide is a broad a_2 absorption band of 2-hydroxy-5-methoxyacetophenone in the form of a salt developed with a maximum at λ 3850 A and ϵ 10000; this maximum is 275 A farther into the long-wave region than the maximum in neutral ethanol; the long-wave edge is 450 A farther into the long-wave region (Fig. 2, Curves 2 and 1). The character of the change in the absorption spectrum of 2-hydroxy-5-methoxyacetophenone in presence of caustic alkali is identical with the effect of alkali on 2-hydroxyacetophenone. Conjugation of the methoxy group in the 5 position with the carbonyl group and the benzene ring is marked by a bathochromic effect.

The action of caustic alkali is not limited to salt formation. It is possible that the sodium atom functions as a hydrogen bridge in the formation of a hydrogen bond between the carbonyl group and the hydroxyl in the 2 position. Investigations of intramolecular compounds with metals [5] showed the possibility of formation of an intramolecular bridge with alkali, alkaline-earth and heavy metals. The structure of the salt of 2-hydroxy-5-methoxyacetophenone may be represented by the formula:



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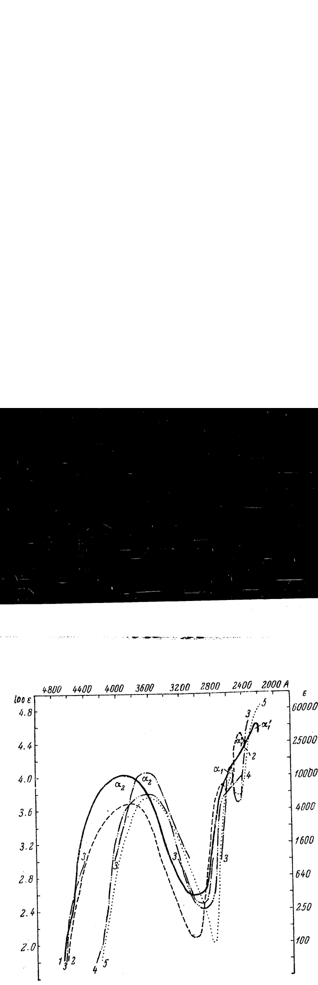

Fig. 2. 1) 2-Hydroxy-5-methoxyacetophenone in ethanol $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M + 100 mol. $NaOC_2H_5$; 2) 2-hydroxy-5-methoxyacetophenone in ethanol $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M + 10 mol. $NaOC_2H_5$; 3) 2-hydroxy-5-methoxyacetophenone in ethanol $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M + 1 mol. $NaOC_2H_5$; 4) 2-hydroxyacetophenone in ethanol $10^{-2}-10^{-4}$ M + 10 mol. $NaOC_2H_5$; 5) 2-hydroxy-5-methoxyacetophenone in ethanol $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M.

The existence of an intramolecular sodium bridge in 2-hydroxyacetophenone is also indicated by the investigations of Hantzsch [6].

The isomeric 2-methoxy-5-hydroxyacetophenone was investigated in ethanol at concentrations of $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M with addition of 10 and 100 mol. sodium ethoxide; the resultant curves of the absorption spectra of the sodium salt of 2-methoxy-5-hydroxyacetophenone were similar to those of the original substance, but the maximum was at λ 3700 A and ϵ 6400, 300 A nearer the long-wave region than the spectrum of the solution in neutral ethanol (Fig. 3, Curves 1 and 2).

In the present case the salt is formed at the hydroxy group in the 5 position, and the change in the spectrum under the influence of caustic alkali is identical with that in the case of 3-hydroxyacetophenone. The conjugation of the methoxy group in the 2 position with the carbonyl group and the benzene ring exerts a bathochromic effect.

2,5-Dihydroxyacetophenone in aqueous and alcoholic solutions of caustic alkali. Aqueous and alcoholic solutions of alkali exert a much greater influence upon the absorption spectrum of 2,5-dihydroxyacetophenone, since both hydroxyls participate in salt formation. Its solutions become deep yellow, orange and brown. 2,5-Dihydroxyacetophenone was investigated in water at concentrations of $2 \cdot 10^{-4}-2 \cdot 10^{-5}$ M with addition of 10 and 100 mol. sodium hydroxide. Addition of 10 mol. sodium hydroxide sharply changes the character of the absorption spectrum of 2,5-dihydroxyacetophenone (Fig. 4, Curve 2). The α_2 band, with a maximum at λ 3800 A and ϵ 2000, is shifted 250 A toward the long-wave region and is 3 times less intense. This α_2 band becomes even broader after addition of 100 mol. sodium hydroxide; its maximum is then at λ 4080 A and ϵ 1600, and it is displaced 280 A nearer the long-wave region with a slight lowering of intensity (Fig. 4, Curve 1). The absorption spectrum of 2,5-dihydroxyacetophenone in water in the region of minimum absorption has superposed on it, both in presence of 10 mol. and of 100 mol. sodium hydroxide, a new absorption band φ with a maximum at λ 2850 and 2960 A and ϵ 7000, corresponding to the hydroquinone band. The α_1 band, on the other hand, is shifted toward the short waves by 395 and 325 A, and the intensities are increased by factors of 1.25 and 1.6 respectively. The absorption bands in alkaline solutions are broader and shallower, indicating superposition of some of the bands.

Fig. 3. 1) 2-Methoxy-5-hydroxyacetophenone in ethanol $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M + 100 mol. $NaOC_2H_5$; 2) 2-methoxy-5-hydroxyacetophenone in ethanol $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M + 10 mol. $NaOC_2H_5$; 3) 2-methoxyacetophenone in ethanol $10^{-2}-10^{-4}$ M; 4) 3-hydroxyacetophenone in ethanol $10^{-3}-3 \cdot 10^{-5}$ M + 100 mol. $NaOC_2H_5$.

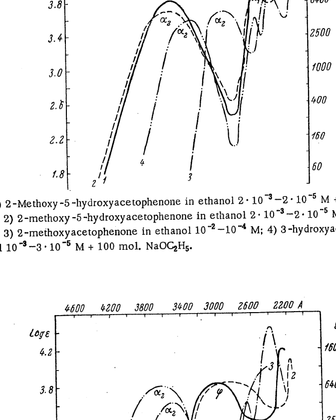

Fig. 4. 1) 2,5-Dihydroxyacetophenone in water $2 \cdot 10^{-4}-2 \cdot 10^{-5}$ M + 100 mol. NaOH; 2) 2,5-dihydroxyacetophenone in water $2 \cdot 10^{-4}-2 \cdot 10^{-5}$ M + 10 mol. NaOH; ; 3) 2-hydroxyacetophenone in ethanol $10^{-2}-10^{-4}$ M + 100 mol. NaOH; 4) 3-hydroxyacetophenone in ethanol $10^{-3}-2 \cdot 10^{-5}$ M + 100 mol. NaOH.

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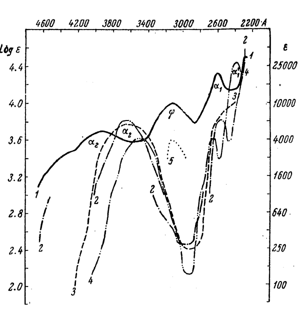
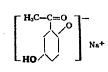
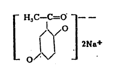


Fig. 5. 1) 2,5-Dihydroxyacetophenone in ethanol $2 \cdot 10^{-4}-2 \cdot 10^{-5}$ M + 10 mol. $NaOC_2H_5$; 2) 2,5-dihydroxyacetophenone in ethanol $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M + 1 mol. $NaOC_2H_5$; 3) 2-hydroxyacetophenone in ethanol $10^{-2}-10^{-4}$ M + 10 mol. $NaOC_2H_5$; 4) 3-hydroxyacetophenone in ethanol $10^{-3}-3 \cdot 10^{-5}$ M + 100 mol. $NaOC_2H_5$; 5) methylhydroquinone in ethanol + 10 mol. $NaOC_2H_5$.

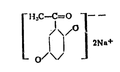
The effect of sodium ethoxide is more strongly manifested in an ethanol solution of 2,5-dihydroxyacetophenone. At a concentration of $2 \cdot 10^{-3}$ M the presence of even 1 mol. sodium ethoxide causes salt formation at the hydroxyl in the 2 position, but 10-fold dilution brings about complete alcoholysis (Fig. 5, Curve 2). At concentrations of $2 \cdot 10^{-4}-2 \cdot 10^{-5}$ M, 2,5-dihydroxyacetophenone in ethanol undergoes alcoholysis on addition of 10 mol. sodium ethoxide, and salt is formed at both hydroxyls; the disodium salt of 2,5-dihydroxyacetophenone gives a very complex absorption curve (Fig. 5, Curve 1) in which the absorption bands are superposed.





The absorption band of the salt of 2,5-dihydroxyacetophenone at the hydroxy group in the 2 position has a maximum at λ 3920 A and ε 5000; subsequently, in the portion of the absorption spectrum between λ 3600 and 2700 A a shallow absorption minimum is formed in the same position as the deep minimum in the spectrum of the salt of 2-hydroxy-5-methoxyacetophenone, since on the latter are superposed the absorption bands of the salt at the hydroxy group in the 5 position with a maximum at λ 3500 A and ε 4000 and the φ band corresponding to the band in the spectrum of the salt of hydroquinone with a maximum at λ 3125 A and ε 10000. The α_1 band of 2,5-dihydroxyacetophenone in ethanol in presence of 10 mol. sodium ethoxide at λ 2600 A and ε 20000 is displaced 50 A toward the short waves in comparison with the α_1 band of 2-hydroxy-5-methoxyacetophenone in presence of 10 mol. sodium ethoxide, and it is 2.5 times more intense than the latter. The incomplete α'_1 band lies at λ 2990 A and ε 32000.

In presence of considerable amounts of caustic alkali, the carbonyl group cannot enter into conjugation with the benzene ring and the hydroxyl groups; the stable ionic form of hydroquinone is formed:



The ionic form of hydroquinone readily changes into quinone, resulting in the appearance in the absorption spectrum of the disodium salt of 2,5-dihydroxyacetophenone of bands corresponding to the bands in the spectra of hydroquinone and quinone. The absorption band characteristic of quinone is superposed on the edge of the α_2 band in the form of an inflection at λ 4300 A and ε 5000. This character of the absorption curve of 2,5-dihydroxyacetophenone also persists after addition of 100 mol. sodium ethoxide to the ethanol solution but this solution is very unstable and quickly darkens and deposits a dark-colored precipitate.

2,5-Dihydroxyacetophenone and its methyl ethers in concentrated sulfuric acid. 2-Hydroxy-5-methoxy-, 2-methoxy-5-hydroxy- and 2,5-dihydroxyacetophenone were examined in concentrated sulfuric acid (d 1.84) at concentrations of $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M. These yellow solutions also start to absorb at λ 4700-4850 A. They all exhibited changes in absorption spectra, leading to strong development of an absorption band α_2 corresponding to the α_2 band of 2-hydroxyacetophenone in concentrated sulfuric acid (Fig. 6).

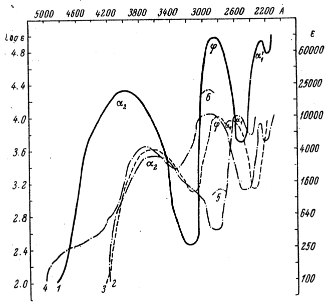


Fig. 6. 1) 2,5-Dihydroxyacetophenone in conc. H_2SO_4 $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M; 2) 2,5-dihydroxyacetophenone in 9.5% H_2SO_4 $2 \cdot 10^{-3}-2 \cdot 10^{-5}$ M; 3) 2-hydroxyacetophenone in 63.4% H_2SO_4 $10^{-3}-10^{-4}$ M; 4) 3-hydroxyacetophenone in conc. H_2SO_4 $10^{-3}-10^{-4}$ M; 5) hydroquinone in conc. H_2SO_4; 6) acetophenone in conc. H_2SO_4.

TABLE 4

Compounds (in solution in sulfuric acid d 1.84)	α_2 band		φ band		α_1 band		α'_1 band	
	λ	ε	λ	ε	λ	ε	λ	ε
2,5-Dihydroxyacetophenone	3970	20000	2830	10000	—	—	2250	80000
2-Hydroxy-5-methoxyacetophenone	4070	6000	2830	12500	—	—	2190	40000
2-Methoxy-5-hydroxyacetophenone	3750	4000	2770	22500	—	—	—	—
2-Hydroxyacetophenone	3580	4000	2830	10000	2665	9000	—	—
2,5-Dihydroxyacetophenone (in ethanol)	3575	6000	—	—	2550	12000	2275	40000

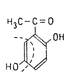
Comparison of the curves of the absorption spectra shows ~~that the~~ spectra of 2,5-dihydroxyacetophenone and its ethers are similar to the absorption spectrum of 2-hydroxyacetophenone in concentrated sulfuric acid, but they differ from it and from the absorption spectrum of 2,5-dihydroxyacetophenone in ethanol by the strong development of the a_2 band, considerably shifted toward the long waves, and by the increased intensity of the absorption especially in the case of 2,5-dihydroxyacetophenone. Participation of the conjugation of the hydroxy and methoxy groups in the 5 position is reflected on the curves of the absorption spectra in concentrated sulfuric acid by the $a_1^!$ band and by the strong bathochromic and hyperchromic effect in comparison with the absorption spectra of 2,5-dihydroxyacetophenone in ethanol and of 2-hydroxyacetophenone in concentrated sulfuric acid. Concerning, however the absorption spectrum of 2,5-dihydroxyacetophenone in concentrated sulfuric acid, monomethylation leads to a hyperchromic effect, the methoxy group in the 2 position causes a 5-fold reduction in the intensity of its a_2 band, while the methoxy group in the 5 position brings about a 3.3-fold reduction in intensity.

The absorption spectra of 2,5-dihydroxyacetophenone and its isomeric monomethyl ethers in concentrated sulfuric acid differ from their spectra in ethanol by the formation of a new band at λ 2830 and 2770 A. A similar band is developed by acetophenone in concentrated sulfuric acid at λ 2950 A and ε 22100 [7]. A band corresponding to the absorption band of acetophenone in concentrated sulfuric acid was also found by N. A. Valyashko and Yu. S. Rozum [4] in the case of 2-hydroxyacetophenone in concentrated sulfuric acid at λ 2830 A and ε 12500.

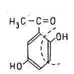
Formation in the absorption spectrum of 2,5-dihydroxyacetophenone in concentrated sulfuric acid of a band corresponding to the acetophenone band appears to indicate that a proportion of the molecules no longer have their carbonyl group in conjugation with the hydroxyls and with the benzene ring, whereas the two hydroxyls in the para position are themselves conjugated with the benzene ring with formation of an absorption band corresponding to the absorption band of hydroquinone in concentrated sulfuric acid with a maximum at λ 2850 A and ε 1250 [8], located in the region of absorption of acetophenone in concentrated sulfuric acid.

Evalation of the Absorption Spectra of 2,5-Dihydroxyacetophenone

In the molecule of 2,5-dihydroxyacetophenone, which gives an absorption spectrum corresponding to the absorption spectrum of 2-hydroxyacetophenone in ethanol but with weaker absorption bands, the carbonyl group may be conjugated with the benzene ring and with one of the two hydroxyl groups separately, as was demonstrated in the preceding communication with reference to 3,5- and 3,4-dihydroxyacetophenones. For 2,5-dihydroxyacetophenone the separate conjugation of each of the two hydroxyls with the benzene ring and with the carbonyl group may be represented by the following scheme:



o-conjugation 1,2



m-conjugation 1,5 (1,3)

From the position of the a_2 absorption bands (λ 3250 A in the case of 2-hydroxyacetophenone and λ 3110 A in the case of 3-hydroxyacetophenone), both conjugations are energetically very similar: 1.2- 92 kcal/mol. and 1.5-88.5 kcal/mol. [9]. Both conjugations in the case of 2-hydroxyacetophenone and 3-hydroxyacetophenone form absorption spectra of one type, very similar among themselves, but the spectrum of 2-hydroxyacetophenone differs from that of 3-hydroxyacetophenone by virtue of the strong development of the bands, of the displacement toward the longer waves, and of their higher intensity. Consequently in the case of 2,5-dihydroxyacetophenone the absorption spectrum corresponding to the spectrum of 2-hydroxyacetophenone predominates, and under the influence of the 1,5-conjugation it undergoes further development, mainly at the a_2 band, the latter being also more intensely absorbed and displaced toward the red.

This feature of conjugation of the carbonyl group with the benzene ring and one of the two hydroxyls persists in 2,5-dihydroxyacetophenone, 2-hydroxy-5-methoxy- and 2-methoxy-5-hydroxyacetophenone in various solvents, in sodium ethoxide and concentrated sulfuric acid. This conjugation is partly suppressed in aqueous and alcoholic solutions of caustic alkali, but conjugation of the two oxygen ions in the para-position is additionally developed with formation of bands corresponding to the hydroquinone bands, while in alcoholic solution the quinone band is also formed. Concentrated sulfuric acid strongly polarizes the molecules of 2,5-dihydroxyacetophenone and its monomethyl ethers, heightens the 1,2 and 1,5 conjugations and partly suppresses the latter with supplementary formation in the absorption spectra of the absorption bands of acetophenone and hydroquinone in concentrated sulfuric acid.

SUMMARY

1. The ultraviolet absorption spectra of 2,5-dihydroxy-, 2-hydroxy-5-methoxy-, 2-methoxy-5-hydroxy- and 2,5-dimethoxyacetophenones were investigated in solution in water, ethanol, dichloroethane, hexane and dioxane, in aqueous and ethanolic solutions of caustic alkali, and in concentrated sulfuric acid.

2. The absorption spectra of 2,5-dihydroxyacetophenone and of its methyl ethers were a complex and correspond to an absorption made up of separate conjugation of the carbonyl group and of the hydroxy and methoxy groups in the 2 and 5 positions with the benzene ring.

3. These 1,2 and 1,5 conjugations are fairly stable and persist in different solvents and in presence of aqueous and ethanolic solution of caustic alkali and in solutions in concentrated sulfuric acid.

4. The conjugation is only partly suppressed in caustic alkali solutions and the latter lead to development of a new conjugation of the para-hydroxyls with the benzene ring, while concentrated sulfuric acid gives rise to an additional conjugation corresponding to acetophenone in concentrated sulfuric acid.

5. The presence of a hydrogen bond between the oxygen of the carbonyl group and the hydroxyl in the 2 position was established in 2,5-dihydroxyacetophenone.

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ENTHALPIES OF FORMATION OF COMPOUNDS OF ZINC WITH ANTIMONY

S. A. Shchukarev, M. P. Morozova and Yu. P. Sapozhnikov

A number of authors [1, 2] have investigated the system zinc-antimony by various methods of physico-chemical analysis. The existence of three separate compounds, ZnSb, Zn_4Sb_3 and Zn_3Sb_2, has been established in this system. The last compound corresponds to the highest melting point.

Oelsen and Middel [3] obtained the enthalpy of formation of ZnSb by the method of direct determination of the heat of mixing of the two metals. The value found was −3.6 kcal/mole.

We prepared the compounds ZnSb and Zn_3Sb_2 by prolonged fusion of the components taken in the appropriate stoichiometric ratio. Fusion was performed in a quartz test tube in an atmosphere of pure argon at a temperature up to 900° with frequent shaking. The alloys were cooled in the furnace for 8-10 hours.

Chemically pure metals, tested by spectroscopic analysis, were utilized for preparation of the alloy. Analysis of the prepared alloys showed that the original composition is substantially unchanged by melting. The lines of the free components were not detected on the x-ray diagrams if the alloys were held at high temperature for a sufficiently long period (8-10 hours). The x-ray diagrams of both products reflected the individuality of their structures.

The enthalpies of formation of both compounds were found by calorimetric determination of their enthalpies of reaction with hydrochloric acid. As in the case of determination of the enthalpies of formation of Mg_3Sb_2 [4] and Li_3Sb [5], the hydrochloric acid for the calorimetric experiments was first reacted with a small amount of the preparation under investigation, so that it contained highly dispersed metallic antimony in suspension. In the present case stibine was not formed in appreciable amount (metallic antimony catalyzes its decomposition) and the reaction of the preparation with hydrochloric acid proceeds quantitatively according to the equations:

$$Zn_3Sb_{2\,cryst.} + 6HCl_{aq} = 3ZnCl_{2\,aq} + 2Sb_{cryst.} + 3H_{2\,gas},$$

$$ZnSb_{cryst.} + 2HCl_{aq} = ZnCl_{2\,aq} + Sb_{cryst.} + H_{2\,gas}.$$

The procedure for the calorimetric experiments has already been described [5]. All the measurements were performed at 25°.

The enthalpies of formation of ZnSb and Zn_3Sb_2 were found as the difference between the enthalpy of reaction of metallic zinc with the acid and the enthalpy of the reaction with acid of the compound.

The value found for the enthalpy of reaction of zinc with hydrochloric acid was −38.9 kcal/g-atom. The compound Zn_3Sb_2 reacts rapidly with hydrochloric acid: the main stage of the calorimetric experiment is completed in 15-20 minutes. The enthalpy values found in three successive experiments were −68.0, −68.4 and −69.7 kcal/mole, giving a mean value of -68.7 ± 0.7 kcal/mole. Deducting the above value for the enthalpy of solution of zinc (−38.9 kcal/g-atom) we obtain for the enthalpy of formation of Zn_3Sb_2 the value of -48.0 ± 1.3 kcal/mole.

$$3Zn_{cryst.} + 2Sb_{cryst.} = Zn_3Sb_{2\,cryst.} + 48.0 \pm 1.3 \text{ kcal.}$$

The compound of Zn with Sb corresponding to the formula ZnSb reacts very much more slowly with hydrochloric acid, so that the main stage of the calorimetric experiment is prolonged and its accuracy is decreased.

The mean value of the heat of reaction based on four successive experiments was -21.1 ± 1.8 kcal/g-mole; hence the enthalpy of formation of ZnSb is -17.8 ± 2.5 kcal/mole:

$$Zn_{cryst.} + Sb_{cryst.} = ZnSb_{cryst.} + 17.8 \pm 2.5 \text{ kcal.}$$

The values found by us for the enthalpies of formation of ZnSb and Zn_3Sb_2 differ very considerably from the values of Oelsen and Middel [3]. This is probably due to the low rate of reaction of zinc with antimony and the short period during which the metals were at a high temperature during the calorimetric experiments of these authors, so that the metals could only react to a slight extent. This explanation appears extremely probable in the light of data [6] for compounds of magnesium with tin and silicon, and also in the light of our observations of the need for prolonged holding of the alloys at high temperature in order to ensure completeness of reaction of both metals. Unfortunately, a considerable proportion of the thermochemical data characterizing intermetallic compounds has actually been obtained by direct determination of the heat of mixing, and this renders them very untrustworthy.

The literature data for the enthalpies of formation of antimony compounds of zinc and cadmium, as obtained by different authors, differ very widely. Biltz and Haase [7] found values of -3 and -4 kcal/mole for the enthalpies of formation of CdSb and Cd_3Sb_2, while the corresponding values of Seltz and de Witt [8] were -3.25 and -7.83 kcal/mole. The enthalpies of formation of the oxides, halides and sulfides of zinc and cadmium, also of their salts with oxygen-containing acids, etc., are all of the same order.

From this standpoint it is of interest to obtain more accurate values of the enthalpies of formation of CdSb and Cd_3Sb_2; it requires to be established whether the values found for them are the result of experimental errors or whether the laws of change of magnitude of the enthalpies of formation of salt-like and intermetallic compounds in one and the same subgroup of the periodic system can indeed be so different.

Dehlinger [9] indicated in 1953 that when an intermetallic system is formed by two metals differing in chemical character, the maximum of the heats of formation (per mean gram-atom) will lie at the compound corresponding to the normal valences of the components; on both sides of this peak the heats of formation change linearly with the composition. Dehlinger thinks this behavior is due to the changing contribution of the bonds to the ionic character with change of composition. We suspect that this linear dependence may be amenable to a more general interpretation not involving any hypothesis about the character of the bond, which cannot always be at all reliably determined.

In a compound whose formula corresponds to the normal valences of both metals, all the bonds that can be formed by their atoms are saturated with atoms of the second component, i.e. the lattice is substantially held together by hetero bonds (bonds between atoms of different elements). In the case of the above-mentioned change of composition, bonds between atoms of different elements are present as well as bonds between atoms of the same element, i.e. the same bonds as in simple substances.

If we assume to a first approximation that the energy of these bonds is the same as in the corresponding atoms, they would not make an appreciable contribution to the value of the enthalpy of formation of the compound.

If this assumption is correct, then, in the case of Zn_3Sb_2 and ZnSb, the enthalpy of formation of the second compound should be about 1/3 of that of Zn_3Sb_2. (In Zn_3Sb_2 all 6 valence electrons of the two atoms of antimony are linked to zinc atoms, whereas in ZnSb only two electrons of the antimony atom can form such bonds.) Actually, 1/3 of the ΔH of formation of Zn_3Sb_2 amounts to -16.0 kcal, while the ΔH of formation of ZnSb, as determined experimentally, is -17.8 ± 2.5 kcal. The mutual influence of the bonds must of course lead inevitably to a more complex dependence of the enthalpy of formation on the composition. In real systems we can expect only a more or less rough approximation to the dependence discussed above, whereas in the system Zn-Sb the dependence is quite pronounced.

Thus, when the maximum of the enthalpy of formation corresponds to the compounds with normal valences, the enthalpies of formation of other compounds of the same elements must be close to the enthalpies of formation of mixtures of this most stable compound with the corresponding element. This similarity between the enthalpies of formation of individual compounds and mixtures of elements with other compounds in a system of two metals is perhaps one of the causes of the frequently observed large number of thermodynamically stable compounds in intermetallic systems.

In nonmetal-metal systems the transition from one compound to another is usually associated with a fairly sharp change in the nature of the chemical bond, with the development of new valence states which place some of the possible compounds energetically in an especially favorable position and exclude other forms which cannot compete energetically with the former. In intermetallic systems, on the other hand, the valence states of the components evidently do not change appreciably with change of composition of the compound, and the nature of the chemical bond does not change sharply with composition.

A second cause of the plentifulness of thermodynamically stable forms in intermetallic compounds is their existence, like the metals themselves, in the crystalline state, so that the difference between the entropies of any one compound and a mixture of this compound with the corresponding element is small. At the same time a factor that results in thermodynamic instability of, for example, many higher oxides, halides and nitrides is absent; that factor is their decomposition into a compound of lower state and a volatile nonmetal, the process being accompanied by a considerable rise in entropy. Now this energetic and entropic comparability of intermetallic compounds and their mixtures, and also of their mixtures with atoms, is possibly one of the causes of the great influence of temperature upon the number of stable forms of compounds which is actually encountered among intermetallic compounds.

The same factor is also partly responsible for those profound differences between the properties of quenched and tempered alloys which are so frequently utilized in practice. Unfortunately, as observed above, we still lack adequate and reliable thermodynamic data for intermetallic systems. This hinders their systematization and generalization.

Still more limited is our knowledge of the values of the entropies of intermetallic compounds.

SUMMARY

1. The enthalpies of formation of ZnSb and Zn_3Sb_2 were determined; they are respectively $-17.8 \pm$ ± 2.5 and -48.0 ± 1.3 kcal/mole.

2. A number of possible causes are discussed for the frequently observed abundance of thermodynamically stable forms in systems metal-metal in comparison with systems metal-nonmetal.

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FORMATION OF SULFIDES BY REACTION OF FERROUS SULFIDE WITH OXIDES OF METALS

II. REACTION OF FeS WITH SiO_2 IN PRESENCE OF CARBON

Zh. L. Vert and M. V. Kamentsev

It was previously shown [1, 2] that reaction between FeS, SiO_2 and C leads to formation of silicon monosulfide according to the equation:

$$SiO_2 + FeS + 2C = SiS + Fe + 2CO. \qquad (1)$$

The reaction, which was investigated up to 1600°, starts in the temperature range of 1100-1300° C and proceeds intensively at 1460° with vigorous evolution of volatile products. The metallic iron formed during the reaction facilitates the reduction of silica according to the equation:

$$SiO_2 + Fe + 2C = FeSi + 2CO. \qquad (2)$$

Formation of ferrosilicon was observed at 1500° [1].

Even when the charge contained a considerable excess of FeS, formation of silicon disulfide was not observed according to the possible equation:

$$SiO_2 + 2FeS + 2C = SiS_2 + 2Fe + 2CO. \qquad (3)$$

On the other hand, reaction of silica with aluminum sulfide [3] proceeds according to the equation:

$$2Al_2S_3 + 3SiO_2 = 2Al_2O_3 + 3SiS_2, \qquad (4)$$

Silicon monosulfide is formed simultaneously if the reaction is performed in a graphite crucible [1], evidently according to the equation:

$$3SiO_2 + Al_2S_3 + 3C = Al_2O_3 + 3SiS + 3CO. \qquad (5)$$

The possibility of formation of SiS_2 by reaction of SiO_2 with FeS has not previously been established.

With the objective of approximate evaluation of the thermodynamic constants of the silicon sulfides, we applied the same method as in the preceding communication [4]. The following were taken as starting data [5]:

$$(\Delta H_{298})_{SiS_2} = -39.0 \text{ kcal/mole; m.p. } 1363° \text{ K and } d_{SiS_2}\ 2.02 \text{ g/cm}^3.$$

On the basis of the rule of additivity of the entropies of solid compounds [6], the entropy of SiS may be assumed to be 8.0 e.u. (entropy units) lower than the value for SiS_2. Here 8.0 is the mean entropy of the sulfur atom, calculated from the entropies of ten different sulfides. The values of ΔH and S of the silicon sulfides taken for the calculations are set forth in Table 1.

At high temperatures a part of the components of Reactions (1) to (5) is in the liquid state and part is in the gaseous state. For calculation of the heat of fusion of the substances, which are not given in thermodynamic tables, a value of 7.3 kcal/mole was taken, and the heats of vapor formation were calculated according to the Truton rule.

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TABLE 1

Values of Thermodynamic Constants of Silicon Sulfides Taken

Sulfide	ΔH_{298} (cal/mole)	S_{298} (e.u.)
SiS	−28900	10.55
SiS_2	−39000	18.55

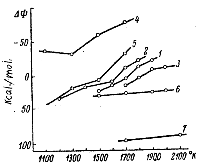

Fig. 1. Change in free energy of Reactions 1,2,3,4,5, 6,7 (numbered as per text).

The change of free energy with temperature of the reactions enumerated is plotted in Fig. 1 (the numbers attached to the plots correspond to the numbers assigned to the reactions in the text). In addition, the dependence of $\Delta\Phi$ on T is shown for the possible secondary reaction:

$$2FeS + C = CS_2 + 2Fe, \qquad (6)$$

and for the reaction in absence of carbon:

$$SiO_2 + 2FeS = SiS_2 + 2FeO. \qquad (7)$$

On the basis of the results of the approximate calculations, the following qualitative conclusions can be drawn. In the reaction between SiO_2 and ferrous sulfide in presence of carbon, silicon monosulfide is first formed. In the same temperature interval the accumulation of metallic iron in the sphere of reaction leads to initiation of the parallel formation of ferrosilicon. With further rise of temperature this process is accompanied, starting from 1850-1900° (1600° C), by formation of SiS_2. By contrast, in the interaction of SiO_2 with Al_2O_3 the exchange reaction associated with evolution of SiS_2 proceeds in a lower temperature region than the formation of SiS. Reactions (6) and (7) are thermodynamically impossible under the reaction conditions.

EXPERIMENTAL

In order to investigate the reaction of silicon dioxide with FeS, two mixtures were prepared which corresponded to the component ratios in Reactions (1) and (3). Their chemical compositions, accounting for admixtures, are given in Table 2. The quartz sand used in the experiment had the following chemical composition (in %): SiO_2 98.62, Al_2O_3 0.85, Fe_2O_3 0.10, moisture 0.11; the characteristics of the FeS and petroleum coke used, are given in [4]. In both cases a 25-30% excess of carbon was used with respect to the amount necessary for the basic reaction and for binding the oxygen of FeO and Al_2O_3.

TABLE 2

Composition of Initial Mixtures

Mixture	Molecular ratios and weight %						
	SiO_2	FeS	C	Fe	FeO	Al_2O_3	Volatiles
I	29.90 1.00	43.77 1.00	16.75 2.80	4.29 0.15	4.08 0.11	0.12 0.002	1.09 —
II	19.66 1.00	57.54 2.00	10.91 2.78	5.63 0.31	5.36 0.23	0.16 0.005	0.74 —

The method of investigation was not different from that described previously [4]. The experimental conditions precluded the possibility that the carbon in the charge might be oxidized by atmospheric oxygen, and this was confirmed by suitable experiments. After the experiment was performed, the residue in the crucible was analyzed for content of Si + SiO_2, boric acid decomposables and in certain cases, iron. The content of SiS and SiS_2 in the volatilized products was calculated by loss of sulfide sulfur and silicon.

Treatment of the reaction product with boric acid solution showed the presence of decomposable sulfides. Their quantity in all the experiments was very minute (up to 3% of the initial sulfide content of the sample). Calculation indicated that the decomposable sulfide was in the form of SiS which, due to various reasons, remained in the reaction mixture; we therefore made a correction in the quantity of silicon dioxide that entered the reaction. To the SiO_2 loss, determined by chemical analysis, was added a quantity of SiO_2 which corresponded to the SiS content of the residue. (The weight of an equivalent amount of CO was accounted for in the calculation).

The difference between the total weight loss and the total weight of the volatilized SiS, SiS_2 and the corresponding quantity of CO, characterized the degree of completeness of Reaction (2). The latter factor enabled the determination of how much of the silicon remaining in the charge was bound with oxygen in the form of SiO_2 and how much with iron in the form of FeSi. The discrepancey in the silicon balance did not exceed 1% with this method of calculation.

It is further necessary to consider the possibility of sulfide sulfur losses, not related to the formation of SiS and SiS_2. At high temperature, vaporization of FeS, and dissociation of FeS and the formation of carbon bisulfide according to Reaction (6) may occur. The thermodynamic probability of the latter reaction taking place, as the data of Figure 1 show, is minute.

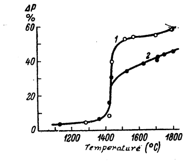

Fig. 2. Loss in weight of reaction mixture upon heating. 1) $SiO_2:FeS = 1:1$; 2) $SiO_2:FeS = 1:2$.

The literature [7] gives data for the dissociation pressure of FeS up to 1400° K, calculated on the basis of experimental data [8], from which it is evident that with increased temperature, change of the vapor pressure of sulfur decreases. Moreover, in our experiments, FeS proved to be a mixed fusion component, which greatly decreased its activity, and, therefore, its dissociation pressure. Several special experiments at 1600-1800° C, performed with a mixture containing a large FeS (SiO_2 : FeS = 1 : 3.3) content did not give a marked increase in the sulfide sulfur loss with respect to the experimental results obtained with Mixture II. Vaporization of FeS should be accompanied not only by sulfur loss but also by a corresponding decrease in iron content.

However, analyses showed that within the margin of experimental error, the iron content of the reaction product corresponded to the initial quantity. All this enables us to assume that the sulfide sulfur loss is caused by the formation of volatile silicon sulfides.

The experimental results from experiments in which the charge contained a molar ratio $SiO_2:FeS = 1:1$, are given in Figures 2 and 3. The curve of weight loss of the samples with respect to temperature sharply rises, starting from ~1430° C. When this temperature is reached, fumes escape through the graphite pores of the crucible and partially precipitate on the cold portion of the angular tube of the Tamman furnace and partially escape through the opening in the stopper, forming a white deposit on its inner surface. The temperature measurements were sometimes hindered, but most of the volatile products exited by the upper part of the tube, enabling us to view the thread of the pyrometer through the opening of the spring washer on the middle of the crucible. The evolution of white fumes in the experiments performed above 1440° C, continued for 35-40 minutes, and then the reaction quieted (in all the experiments, the charge was kept at the given temperature for 1 hour). The curve of weight loss of the charge above 1500° C is almost horizontal and shows a slight rise only at 1800°.

The curve of the variation of the yield of SiS with respect to temperature (Figure 3) also has the same form as the above curve; there is a sharp jump in this curve above 1410° C. When the temperature is further raised from 1500 to 1800°, the yield of SiS increases more slowly. This is due to the fact that a part of the SiO_2 reacts according to Reaction (2) with the formation of FeSi and the further formation of SiS proceeds according to reaction:

$$FeSi + FeS = SiS + 2Fe. \qquad (8)$$

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Fig. 3. Variation of the distribution of silicon in the reaction products with respect to temperature (SiO_2 : FeS = 1 : 1).

Fig. 4. Variation in the distribution of silicon in the reaction products with respect to temperature (SiO_2 : FeS = 1 : 2).

The formation of ferrosilicon was noted, starting from 1400° C. Its content in the reaction products in this series of experiments, reached a maximum at 1440°, after which is gradually decreased and fell to zero approximately at 1850-1900° C.

Heating of the charge at 1800° caused the loss of ferrous sulfide (in moles) exceeding the quantity of SiO_2 lost. Probably, a small quantity of SiS_2 formed at this point.

The data obtained in experiments with Mixture II (SiO_2 : FeS = 1 : 2) , are given in Figures 2 and 4. As in the first series of experiments, heating of the reaction mixture to 1420-1440° C caused the evolution of white fumes. The weight of the charge sharply decreased in this temperature interval.

The yield of SiS up to 1600° C was the same in both series of experiments. The excess of FeS did not affect the formation temperature of the monosulfide. Starting from 1620°C, the yield of SiS fell due to the formation of SiS_2, the content of which was quite considerable in the volatilized products at 1700-1800°.

TABLE 3

Comparison of Calculated and Experimental Formation Temperatures of Compounds in the System SiO_2–FeS–C

Compound	Formation temperature	
	calculated	experimental
FeSi	1340°	1400-1420°
SiS	1455	1420-1450
SiS_2	1610	1650-1700

The region in which ferrosilicon was present proved to be independent of the concentration of ferrous sulfide: FeSi started to form at about 1400° and practically disappeared at 1900° due to the course of Reaction (8). It must be noted that the completeness and rate of the latter process, apart from concentration, depends in great degree on the contact conditions of the two liquid layers – that of the metallic fusion and the sulfide slag.

With respect to our thermodynamic calculations for the system SiO_2–FeS–C, at a sufficiently high temperature, formation of SiS with SiS_2, we found, is possible. In Table 3, a comparison of the calculated and experimental formation temperatures of FeSi, SiS and SiS_2 is presented. (By formation temperature, we mean the temperature at which the $\Delta\Phi$ of the reaction is equal to zero; by the experimental temperature, we mean the region of sharp rise of the curve of the yield of the corresponding component). The value for FeSi is calculated for the case of the presence of free iron in the initial mixture.

Taking into consideration the approximate character of the calculations, the agreement between the results may be considered completely satisfactory.

SUMMARY

1. The reaction between SiO_2 and FeS in presence of carbon commences at about 1100° C. Starting from 1450°, the reaction goes violently and is accompanied by evolution of the volatile sulfide SiS regardless of the FeS : SiO_2 ratio.

2. It is shown that at sufficiently high temperature (above 1600°), SiS_2 is formed at the same time as SiS. The results of experiments in this direction confirmed the preliminary thermodynamic calculations.

3. Commencing from 1400° C, reduction of SiO_2 to metal is observed in presence of iron with formation of FeSi. At a temperature above 1500° C, in presence of ferrous sulfide, the silicide decomposes with formation of silicon sulfide.

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HYDROLYSIS OF SALTS

I. PERCHLORATES OF ELEMENTS OF THE SECOND GROUP OF THE PERIODIC SYSTEM

L. S. Lilich and M. E. Mogilev

If solutions are regarded from the standpoint of D. I. Mendeleev (as chemical systems formed by interaction of solvent with dissolved substance [1]), we should expect solution to be accompanied by a change in a number of properties not only of the dissolved substance but also of the solvent. The studies of A. Werner [2] on aquo- and anhydro acids and bases point at a possible change in the solvent, in particular water, due to dissolution of electrolytes and some complex compounds.

Developing the ideas of A. Werner and L. A. Chugaev, A. A. Grinberg [3] and his co-workers succeeded in establishing a relation between the electrostatic and polarizing property of components and the properties of the solvo-acids and bases formed.

In the present investigation an attempt is made to establish, in the light of the periodic law, a relation between the properties of aquo-acids (in the first instance, their strength) formed by hydration of some ions and their chemical composition. The ideas governing our work in this direction are those stated by D. I. Mendeleev about the periodic law as a universal law of chemistry [1, 4] and its significance for solutions. To quote his words [5]:

"It seems to me, although certainly not yet proven, that for the study of properties of even such complex substances as solutions by comparison of the change of properties with change of equivalent or particle weights, we must have an orderly system of complex substances similar to that available for elements on the basis of their atomic weights."

As the first stage in our program of investigation we have studied the hydrolysis of perchlorates of elements of the second group of the periodic system. We chose perchlorates because the ClO_4^- ion possesses only a very slight tendency to complex formation [6], and in the present case complex formation would have complicated the problem. Other advantages of perchlorates of elements of the second periodic group are the constant valence of the cation (excluding mercury), their high solubility, and the absence of precipitate from the solutions.

As the main criterion of the strength of the aquo-acids formed, we took the change of activity of the hydrogen ions in the solutions examined. In this connection we assumed that the scheme of dissociation of these acids proposed by A. Werner is perfectly adequate.

Many studies on hydrolysis of salts have appeared in the literature; there are, however, hardly any systematic investigations with selected ions over a wide concentration range. The most interesting for our purposes was the paper of Reiff [7] in which the author attempts to correlate the phenomena of hydrolysis of some hydrated ions with their ionization potential. Although the author appreciated the importance of the problem, he did not pay sufficient attention to the role of anions, due to which some of his conclusions call for revision.

Cupr and co-workers [8, 9, 10] made a study of the hydrolysis of perchlorates; however, these authors did not systematize their results. Some workers have studied the hydrolysis constants, but the value of their results is limited by the narrow interval of concentrations, which is bound up with the previously proposed reaction mechanism.

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EXPERIMENTAL

The perchlorates of the cations which we studied were prepared by reaction of perchloric acid with the corresponding oxides or hydroxides. The perchloric acid was purified by the method that Yu. Karyakin described [11], and the oxides and corresponding hydroxides were of analytical grade. Solution of the oxides (hydroxides) was carried out in the presence of a deficit of perchloric acid. The solution with the precipitate was evaporated down almost to dryness in a porcelain cup and traces of heavy metal ions were precipitated due to the presence of the alkaline medium.

After dilution with water, the solution was filtered through a porous filter No. 4 and the filtrate was weakly acidified with perchloric acid. Qualitative tests for the presence of Cl^-, SO_4^{--} and Fe^{+++} ions gave negative reactions. From this filtrate, the perchlorate was obtained by 3-fold recrystallization (upon separation of the crystals from the mother liquor, it was sucked through a Buchner funnel in the course of several hours).

Beryllium perchlorate was recrystallized without heating in a vacuum-desiccator over phosphoric anhydride. In two cases, the perchlorates were prepared by another method; thus, for example, zinc perchlorate was prepared by the reaction of zinc sulfate (recrystallized several times) with an equivalent amount of pure barium perchlorate, and mercury perchlorate (II) was prepared by the reaction of vacuum-distilled mercuric chloride (II) with silver perchlorate (recrystallized several times).

As a result of the work, it was clear that the general method which we selected for preparing the perchlorates was quite satisfactory for our purposes.

The pH was measured by a glass electrode, prepared from Mac Innes glass as V. A. Pchelin described [12]. Calibration was carried out with the aid of buffer mixtures in the pH interval 2-8. In more acid solutions the calibration was performed with perchloric acid of a given concentration, taking into account the average activity coefficient of the hydrogen ion [13]. The glass electrode was located in the same vessel as the solution, and it was connected to a saturated calomel electrode through an intermediate solution (saturated solution of $NaNO_3$). The electrochemical cell was thermostatically regulated in an oil thermostat at a temperature of $25 \pm 0.1°$. Measurements were taken with the aid of a potentiometer, type PPTV-1 and a specially constructed amplifier which worked on the principle of the Wheatstone bridge with pentode 6Zh1Zh. The sensitivity of the galvanometer was 10^{-8} A/mm, and the sensitivity during measurements was 0.1 mV. Equilibrium was considered to be established if in the course of 1 hour, the measurements did not diverge more than 0.2 mV.

The figures given for the hydrogen-ion activity are given without taking into account the diffusion potentials, the evaluation of which in our case was very difficult. The possibility of such an allowance was seen as follows. The results which we obtained, as a rule, coincided with the literature data; in particular, there was good agreement with the data of Reiff [7], who in determining the hydrogen ion activity by measuring the e.m.f. (in the presence of diffusion potential) as well as by a polarization method, came to the conclusion that even in concentrated solutions there is a satisfactory agreement in results. Moreover, we considered that for the given problem of comparing pH magnitudes with respect to solutions of the same composition, and containing ions of approximately the same mobility (the exceptions are Be^{++} and Hg^{++}, on which there is no data), the suggested approximation is permissable even if these values diverge from the real ones.

All the solutions were made up by weight and their concentrations are expressed as molarities ($\bar{m}$). We used twice distilled water with pH 6.8-6.95. Less concentrated solutions were prepared always by dilution of the more concentrated. Analysis of the initial substances and the initial solutions was performed only on the cation. The analysis was performed according to the methods described by Gillebrant and Lendel [14]: Be – by the method of weighing the oxide, Mg – by the pyrophosphate method, Ca – by the permanganate method, Sr and Ba –by the sulfate method, Zn–by the ferrocyanide method, Cd–by weighing the sulfate, and Hg–by the thiocyanate method.

Our resulting measurements are given in Figure 1 and in Tables 1 and 2, from which it is first of all evident in all cases that as the concentration of the perchlorates increases, the acidity of the solutions increases. In some cases, as for example, mercury perchlorate, it reached the magnitude characteristic of strong acid solutions. This, undoubtedly, is of interest from the theoretical as well as the practical standpoint.

An exposition of the reasons for the increased acidity, in our opinion, is very difficult since along with the increase of concentration of the centers that act on the ever decreasing quantity of water molecules, upon

increase of the salt concentration, a whole series of complex reactions takes place which lead to polymerization of the cations [15, 16], complex-formation, change of coordination number etc.

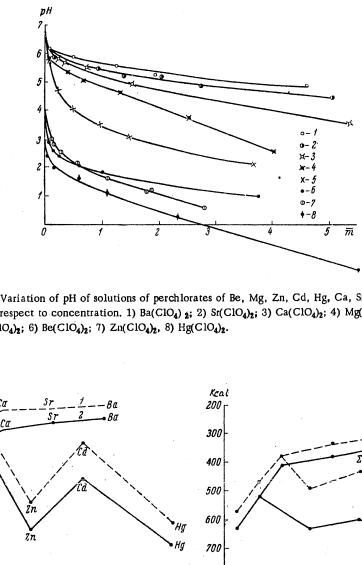

Fig. 1. Variation of pH of solutions of perchlorates of Be, Mg, Zn, Cd, Hg, Ca, Sr, and Ba with respect to concentration. 1) $Ba(ClO_4)_2$; 2) $Sr(ClO_4)_2$; 3) $Ca(ClO_4)_2$; 4) $Mg(ClO_4)_2$; 5) $Cd(ClO_4)_2$; 6) $Be(ClO_4)_2$; 7) $Zn(ClO_4)_2$, 8) $Hg(ClO_4)_2$.

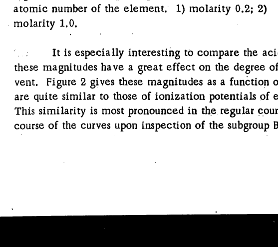

Fig. 2. Variation of pH of perchlorate solution with the atomic number of the element. 1) molarity 0.2; 2) molarity 1.0.

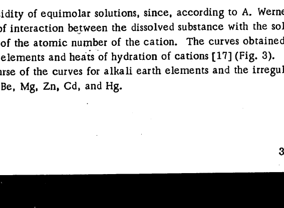

Fig. 3. Variation of the hydration energy (L) and the ionization potential (Σ I) with the atomic number of the element.

It is especially interesting to compare the acidity of equimolar solutions, since, according to A. Werner, these magnitudes have a great effect on the degree of interaction between the dissolved substance with the solvent. Figure 2 gives these magnitudes as a function of the atomic number of the cation. The curves obtained are quite similar to those of ionization potentials of elements and heats of hydration of cations [17] (Fig. 3). This similarity is most pronounced in the regular course of the curves for alkali earth elements and the irregular course of the curves upon inspection of the subgroup Be, Mg, Zn, Cd, and Hg.

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TABLE 1

$Ca(ClO_4)_2$		$Sr(ClO_4)_2$		$Ba(ClO_4)_2$	
$\overline{m}$	pH	$\overline{m}$	pH	$\overline{m}$	pH
0.232	5.82	0.155	5.84	0.0558	6.15
0.326	5.70	0.914	5.48	0.478	5.85
0.731	5.49	1.384	5.21	1.255	5.61
1.523	4.90	2.02	5.20	1.915	5.17
5.380	3.53	2.74	4.85	4.581	4.85
		5.05	4.44		

TABLE 2

$Be(ClO_4)_2$		$Mg(ClO_4)_2$		$Zn(ClO_4)_2$		$Cd(ClO_4)_2$		$Hg(ClO_4)_2$	
$\overline{m}$	pH	$\overline{m}$	pH	$\overline{m}$	pH	$\overline{m}$	pH	$\overline{m}$	pH
0.00217	3.95	0.0430	5.90	0.101	3.03	0.0155	6.19	0.0000817	4.43
0.0183	3.35	0.392	5.33	0.137	2.85	0.0444	5.74	0.000311	3.74
0.0726	2.91	0.667	5.08	0.263	2.56	0.204	4.73	0.00117	3.28
0.135	2.57	1.30	4.64	0.520	2.15	0.461	4.11	0.00172	3.14
0.251	2.40	2.51	3.78	1.086	1.65	0.946	3.54	0.0045	2.94
0.594	2.04	4.00	2.51	1.76	1.20	1.47	3.08	0.0187	2.63
1.00	1.81			1.85	1.26	3.67	2.12	0.0458	2.40
3.76	0.97			2.79	0.64			0.0840	2.22
								0.157	2.04
								0.576	1.64
								1.08	1.13
								2.32	0.3
								5.51	−1.56

The assertion of certain authors [18] that for normally dissociated zinc, cadmium and mercury salts, hydrolysis is greater in passing from zinc to mercury, is incorrect.

The curves showing the sum of the ionization potentials, heats of hydration and pH of solutions of investigated elements, clearly indicate the phenomenon of secondary periodicity, first noted by E. V. Biron [4, 19-22]. This curious fact of the similarity of the above curves primarily indicates that the degree of deformation of the water molecules primarily depends on the ionization potential of the cation to which the water molecule attaches itself, thereby lessening the internal energy of the former. As we know, the similarity between ionization potentials and heats of hydration was noted also by Bernal [23]. The absence of complete parallelism, undoubtedly indicates the more complex nature of the described phenomena and their dependence on other magnitudes relating to the ionic radius, the effective nuclear charge and the structure of the atom.

The considerable change in the water molecules, as a result of solution of the cited salts, is reflected in the properties and energetics of the solvent and the solute, making it necessary to take these factors into consideration when studying the properties of these substances.

SUMMARY

1. The acidity of aqueous solutions of perchlorates of cations of the second group of the periodic system of elements rises with increasing concentration.

2. The acidity of equimolar solutions of perchlorates of the investigated cations changes in parallel with the change of their ionization potential, due to which the development of secondary periodicity (closely associated with the ionization potential) is also manifested in the hydrolysis of these salts.

3. The phenomena described above can be explained by the concept of aquo-acids which are formed by hydration of the ions.

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HYDROLYSIS OF SALTS

II. HALIDES OF ZINC, CADMIUM AND MERCURY

L. S. Lilich and Yu. S. Varshavsky

In the preceding communication [1], which dealt with the hydrolysis of perchlorates of elements of the second group of the periodic system, attention was drawn to a relation between the ionization potential of the elements and the acidity of their perchlorate solutions. It was also pointed out that perchlorates were actually selected deliberately for the investigation in order to rule out the influence of complex formation on the hydrolysis of those salts. For theory and practice, however, no less interest is attached to the study of the influence of anions upon the hydrolysis of salts; in the present investigation we have therefore attempted to clarify the influence of anions of halides of the same Group II elements, which are characterized by interaction with the anions in question (Hg, Cd and Zn).

Anions of halides are also convenient objects for study in that they permit a correlation of hydrolysis with the periodic law not only in regard to cations, as was already done [1], but also in regard to anions. Special attention is given here to the hydrolysis of zinc salts because the behavior of zinc toward halide ions has not previously been fully clarified, and the solubility of its salts enables an investigation to be undertaken over a wider range than for the other two ions.

A systematic study of these salts (also of perchlorates) has been made by Reiff [2]. This author, however, drew some faulty conclusions from his work due to erroneous concepts of the influence of anions.

EXPERIMENTAL

The method of determining hydrogen ion activity was described previously [1].

Zinc chloride was prepared by two methods: by vacuum-distillation of chemically pure $ZnCl_2$ [3] and the method described by Yu. V. Karyakin [4]. Zinc bromide was prepared by dissolving chemically pure zinc oxide in hydrobromic acid [5]. Zinc iodide was prepared by the method described by Yu. V. Karyakin [4]. Zinc nitrate was purified by 3-fold recrystallization of the chemically pure compound.

Cadmium chloride was prepared from cadmium carbonate which in its turn, was prepared from cadmium sulfate by precipitation with hydrogen sulfide, solution of the sulfide with hydrochloric acid, and finally, by precipitation of $CdCO_3$ by means of $(NH_4)_2CO_3$. After the compound was dried, cadmium chloride was vacuum-distilled (1 mm at 700°). Cadmium bromide was prepared by the same method and was purified by vacuum-distillation.

Cadmium iodide was purified by repeated recrystallization of the chemically pure compound, since it showed signs of decomposition during distillation.

Mercuric chloride (II) and bromides (II) of mercury were prepared from mercuric oxide of analytical grade, by solution in chemically pure hydrochloric or hydrobromic acids; after drying over P_2O_5, the resulting crystals were vacuum-distilled in the same manner as cadmium chloride. The mercuric iodide (II) used was of analytical grade.

Analyses of all salts other than nitrates were performed for the cation and anion. The results agreed with the stoichiometric ratios within the range of experimental error. The halogen ion was determined by potentiometric titration by means of $Hg_2(NO_3)_2$, and the iodine – by means of $AgNO_3$ by the method that Koltgof described [6]. The cations were determined in the same manner as in the preceding work [1].

Our results are given in Figures 1-5 and in Tables 1-3. From Figures 1-3, which give the variation of the pH for the above salts with respect to their molar concentration, it is evident that as their concentration increases, the acidity of the perchlorate as well as the halide salts of the above elements, increases. A similar phenomenon was noted by E. Newbery [8]. The explanation of this is, probably, the same as was given previously [9].

Figures 1-3 show that in all three cases, the perchlorates of the corresponding elements always give a more acid reaction, at comparable concentrations, than the corresponding halides. Therefore, the belief of various authors [7] that the acid reaction of the zinc salts is caused by complex-formation, is erroneous, since in the case of the perchlorates there is a more acid reaction than in the case of the halides. Similar phenomena were noted in cases with aluminum [9], iron [10] etc.

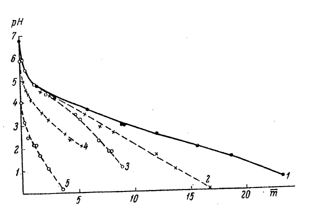

Fig. 1. Variation of pH with concentration for $ZnCl_2$ (1), $ZnBr_2$ (2), ZnI_2 (3), $Zn(NO_3)_2$ (4), $Zn(ClO_4)_2$ (5).

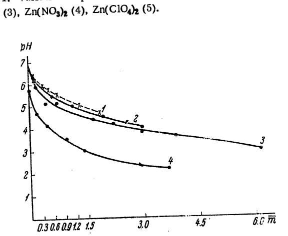

Fig. 2. Variation of pH with concentration for CdI_2 (1), $CdBr_2$ (2), $CdCl_2$ (3), $Cd(ClO_4)_2$ (4).

We believe that Werner's theory accounts for the above fact since the anion that attaches itself to the central ion primarily affects the charge of the latter, thus greatly altering the strength of the bond between the complex ion and the solvent molecules, entering into the inner sphere of the complex. The degree of deformation of the solvent molecules is thus altered, i.e. the strength of the aquo-acid. The explanation of the effect of the anion and the concentration given by Reiff [2], seems incorrect to us, since it contradicts the statements of Werner [11] on aquo-acids, although Reiff himself bases his argument Werner's theory.

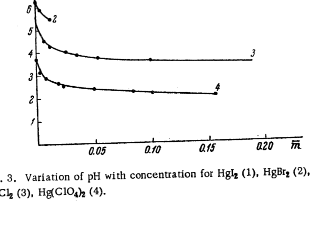

Fig. 3. Variation of pH with concentration for HgI_2 (1), $HgBr_2$ (2), $HgCl_2$ (3), $Hg(ClO_4)_2$ (4).

TABLE 1

$ZnCl_2$		$ZnBr_2$		ZnI_2		$Zn(NO_3)_2$		$Zn(ClO_4)_2$	
$\bar{m}$	pH	$\bar{m}$	pH	$\bar{m}$	pH	$\bar{m}$	pH	$\bar{m}$	pH
0.035	6.45	0.024	6.72	0.156	5.88	0.022	5.85	0.052	4.07
0.125	5.95	1.78	4.48	1.29	4.80	0.155	4.95	0.198	3.22
0.397	5.40	2.53	4.37	2.34	4.40	0.408	4.54	0.556	2.50
1.350	4.75	3.09	4.20	3.39	4.18	0.613	4.42	1.15	2.13
1.636	4.70	5.64	3.45	4.91	3.48	0.920	4.15	1.11	2.10
2.780	4.35	7.07	2.92	5.14	3.25	1.88	3.55	2.32	1.12
4.10	4.05	8.23	2.64	6.81	2.27	2.38	3.24	3.50	0.14, 0.20*
4.88	4.02	12.00	1.60	7.79	1.78	3.93	2.63	4.91	−0.40, −0.28*
5.98	3.61 *	13.59	0.94	7.90	1.75	5.22	2.12		
9.13	2.92	16.70	0.05, 0.10*	8.85	1.03				
12.07	2.50, 2.50 *								
15.64	1.93, 1.93 *								
18.62	1.50								
23.30	0.50, 0.55*								

TABLE 2

$CdCl_2$		$CdBr_2$		CdI_2	
$\bar{m}$	pH	$\bar{m}$	pH	$\bar{m}$	pH
0.193	6.03	0.09	6.30	0.118	6.34
0.242	5.90	0.150	6.22	0.162	6.19
0.386	5.15	0.288	5.97	0.253	6.03
0.738	5.20	0.320	5.94	0.316	5.94
1.12	4.85	0.426	5.77	0.441	5.82
1.70	4.44	0.602	5.47	0.515	5.70
2.27	4.17	1.005	5.06	0.733	5.52
3.90	3.58	1.964	4.52	1.38	5.09
6.18	2.93	3.00	3.97	1.933	4.76

TABLE 3

$HgCl_2$		$HgBr_2$		HgI_2	
$\bar{m}$	pH	$\bar{m}$	pH	$\bar{m}$	pH
0.00795	4.42	0.000567	6.22	0.00013	6.55
0.0115	4.26	0.00315	6.13		
0.0212	4.27	0.00255	5.83		
0.0268	4.02	0.00591	5.47		
0.0359	3.90	0.00737	5.46		
0.0541	3.77	0.01208	5.48		
0.1040	3.65				
0.1905	3.47				

* Measurement of pH by hydrogen electrode.

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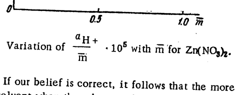

Fig. 4. Variation of $\frac{a_{H^+}}{\bar{m}} \cdot 10^5$ with $\bar{m}$ for $Zn(NO_3)_2$.

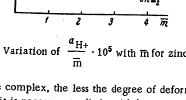

Fig. 5. Variation of $\frac{a_{H^+}}{\bar{m}} \cdot 10^5$ with $\bar{m}$ for zinc halides.

If our belief is correct, it follows that the more stable the complex, the less the degree of deformation of the solvent when the other conditions are constant. However, it is necessary to distinguish between the stability of the bond between addendum and central ion and the stability of the complex as such in the given medium. The latter is characterized by an equilibrium constant, which, as we know, is a function not only of the stability of the bond, but also of entropy and temperature.

The necessity of distinguishing between the above stabilities is especially apparent in those cases when the central ion does not exhibit a typical tendency to simple hydration or to strong complex-formation, i.e. when it is impossible to disregard one or the other factor as negligible. The elements which we selected, particularly zinc, were very characteristic in the sense that their ions are of an intermediate character between the typical complex-formers and typical ions, which are subject only to hydration.

The results obtained corroberate our hypothesis of the effect of anions on the strength of aquo-acids, in that the acidity in all three cases decreases with increase of the stability constant of halide complexes.

If, in the case of mercury and cadmium there is a characteristic increase of the stability constant of the complex in passing from chorine to iodine, the reverse is true of zinc (a reverse order of stability), and the variation in the acidity of the corresponding solutions is in perfect agreement with this fact.

The attempt of certain authors to relate, in similar instances, the order of acidity to only the properties of the anion [12] is valid only for special cases, since the acidity of the solution is determined by the total interaction of the properties of the system under examination.

It is not true that our conception of the effect of complex-formation entirely represents the full complexity of the phenomena taking place in solutions; however, our hypothesis satisfactorily explains a number of facts related to the solution of the above salts. For example, the fact that solutions of zinc nitrate differ greatly in acidity from solutions of the perchlorate (Figure 1), undoubtedly indicates that side by side with complex-formation, the acidity is determined by still other factors that are dependent on the nature of the anion as well as the cation (the NO_3^- ion has a greater tendency towards complex-formation than has the ClO_4^- ion) [13]. It must be noted that there is a sharp differentiation in the acidity of the solutions of the halides of mercury and cadmium (starting from the lowest concentrations), depending upon the anion, but with zinc halides, the differentiation begins only at high concentrations (at molarities >4), which is also explainable on the basis of the differing tendency of the above cations towards complex-formation, since the stability of the halide complexes increases in passing from zinc to mercury.

At a concentration less than 4 M, the following relationship may be written for the halides of zinc: $a_{H^+} \cdot 10^5 = 0.30\ \bar{m}^2 + 0.85\ \bar{m}$ ($\bar{m}$ – molarity); or for low concentrations: $a_{H^+} \cdot 10^5 = 0.85\ \bar{m}$ (Fig. 4).

For zinc nitrate, this expression takes the following form: $a_{H^+} \cdot 10^5 = 6.67\ \bar{m}$ (Fig. 5).

Similar expressions were also derived by other authors [14-16].

SUMMARY

1. The acidity of solutions of halides of zinc, cadmium and mercury rises with increasing concentration.

2. A comparison of the acidity of equimolar solutions of perchlorates with that of solutions of halides of the above metals reveals that the halides are less acidic than the perchlorates. One of the main causes of this is complex formation of the cations with halogens.

3. Individual comparison of the acidity of equimolar solutions of halides of zinc, cadmium and mercury established a parallelism between the stability of the complex formed between the cation and the respective anion and the acidity of the corresponding solution. Increase in the stability of the complex leads to fall in acidity, and this "reversal of the stability series" is also reflected in the hydrolysis of the salts that we investigated.

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DIPOLE MOMENTS OF SOME COMPLEX COMPOUNDS OF TITANIUM AND TIN TETRACHLORIDES. VII

O. A. Osipov

The dipole moment is enormously important, as a quantitative characteristic of the polarity of a molecule, for determination of spatial structure and for clarification of the nature of the chemical bond and the mutual influence of atoms.

In the chemistry of complex compounds the determination of dipole moments not only permits the establishment of the spatial structure of the complex as a whole but also the spatial distribution of the substituents. The literature data on the dipole moments of complex compounds have been collected and systematized in the publication of I. A. Sheka [1]. Somewhat earlier, a review paper devoted to the dipole moments of inorganic compounds have been collected and systematized in the publication of I. A. Sheka [1]. Somewhat earlier, a review paper devoted to the dipole moments of inorganic compounds was published [2]. Very few papers have been published on measurements of dipole moments of complex compounds. Most of these relate to complex compounds of halides of titanium and tin.

Investigation of complex compounds of halides of elements of Group IV of the periodic system with various organic and inorganic addends is not merely of theoretical interest, since it can have practical value in organic synthesis. We know, for example, that the catalytic action of $TiCl_4$ and $SnCl_4$ in polymerization reactions is due to the formation of intermediate complex compounds of them with reaction components or with activators (co-catalysts) of polymerization [3, 4]. From this standpoint the determination of the composition, structure and stability of complex compounds of halides of tin and titanium with diverse organic compounds presents definite interest. The present paper deals with the determination of the dipole moments of complex compounds of tin and titanium tetrachlorides with ethyl, isobutyl and isomyl esters of butyric acid with the objective of clarification of their nature.

We employed the methods of physico-chemical analysis for establishment of the composition of the prepared complexes. We examined the viscosity, fusibility, electrical conductivity and density of the systems: $TiCl_4-C_3H_7COOC_2H_5$, $TiCl_4-C_3H_7COOC_4H_9$, $TiCl_4-C_3H_7COOC_5H_{11}$, $SnCl_4-C_3H_7COOC_2H_5$, $SnCl_4-C_3H_7COOC_4H_9$ and $SnCl_4-C_3H_7COOC_5H_{11}$, as functions of the composition and at a series of temperatures. Our results showed that $TiCl_4$ forms compounds with one molecule of ester, while $SnCl_4$ forms compounds with two molecules of ester. These findings are in harmony with the results of previous investigations [5-7].

EXPERIMENTAL

The dielectric permeability was determined by the beat method at a frequency of $5 \cdot 10^5$ hertz in a thoroughly sealed liquid condenser with cylindrical electrodes with a capacity of $15.5 \mu\mu F$. The cell was calibrated against benzene $\epsilon_{20°}$ = 2.2830) and against chlorobenzene ($\epsilon_{20°}$ = 5.686). The substances used for calibration were thoroughly purified. Measurements were carried out at $20 \pm 0.1°$. The density was determined with a pycnometer with a finely graduated stem. The refractive index was determined with an Abbe refractometer equipped with a thermostatic device. From the dependence of the dielectric permeabilities and densities on the concentration in benzene at 20°, the magnitudes of the polarization (P_2) of the dissolved complexes were found, and these values were extrapolated to infinite dilution (P_∞). The dipole moments were calculated from the formula: $\mu = 0.012813 \sqrt{(P_\infty - P_D)T}$.

We determined the electrode polarization P_e from the refraction of the complex compounds that we investigated. We assumed that the atomic polarization was 15% of the molar refraction, as was assumed by other investigators [8].

In view of the fact that the prepared complex compounds of $TiCl_4$ and $SnCl_4$ are extremely difficult to purify, we prepared benzene solutions of the complexes by starting from stoichiometric amounts of the halide of Ti or Sn and the appropriate ester.

The substances used in the research were purified in the following manner: Benzene ("cryoscopic" grade) was kept for several days over metallic mercury in order to remove any traces of sulfur. It was then dried for a long period over metallic sodium, and finally distilled over sodium. The fraction taken for the experiments had b.p. 79.9-80.1° at normal pressure, n_D^{20} 1.5013, and d_4^{20} 0.8789. Titanium tetrachloride was kept for several days over metallic mercury and distilled over the latter through a special separator 1/5 filled with mercury. The product purified in this manner had b.p. 136.4° (760 mm), d_4^{20} 1.7273.

We prepared tin tetrachloride by the method of Lorenz [9]. The product was distilled over metallic tin in order to bind traces of chlorine. After a second distillation a product with b.p. 113.4-114° and d_4^{20} 2.2326 was obtained.

The ethyl, isobutyl and isoamyl esters of butyric acid were washed with sodium carbonate solution and dried with freshly calcined calcium chloride before being subjected to fractional distillation.

Fractions boiling in the following ranges were taken:

		d_4^{20}	n_D^{20}
$C_3H_7COOC_2H_5$	120.4-121°	0.8780	1.3930
$C_3H_7COOC_4H_9$	156.6-157	0.8662	1.4035
$C_3H_7COOC_5H_{11}$	178.3-178.8	0.8672	1.4105

All the purified substances were stored in sealed ampoules. During the preparation of solutions, all possible precautions were taken to prevent access of moisture.

DISCUSSION OF RESULTS

Complex compounds of titanium tetrachloride. The complex compounds formed by $TiCl_4$ with ethyl, isobutyl and isoamyl esters of butyric acid are crystalline substances. The light-yellow crystals are highly soluble in benzene, and they are decomposed by water. Melting points of complexes: $TiCl_4 \cdot C_3H_7COOC_2H_5$ 103.0°; $TiCl_4 \cdot C_3H_7COOC_4H_9$ 78.5° and $TiCl_4 \cdot C_3H_7COOC_5H_{11}$ 70.3°.

The data show that the melting point falls considerably with increasing size of the alcohol radical in the ester. A similar phenomenon was observed [10] during investigation of systems formed by tin tetrachloride with esters of monobasic acids.

In Tables 1-3 are set forth the results of measurements of the dielectric permeability (ϵ), density (d) and the calculated values of the polarization (P_2) of complex compounds of titanium tetrachloride with the ethyl, isobutyl and isoamyl esters of butyric acid in dependence on the molar ratios of components. For the first complex the polarization, extrapolated to infinite dilution $P_{2\infty}$, was 500 cc, while the deformation polarization ($P_D = P_E + P_A$) was 76.5 cc. For the second and third complexes these magnitudes were respectively 499 and 87.28, 496 and 93.40 cc. We calculated the dipole moments from the orientated polarization ($P_0 = P_{2\infty} - P_D$) by the above mentioned formula of Debye, and we obtained the following values: $TiCl_4 \cdot C_3H_7COOC_2H_5$ 4.52, $TiCl_4 \cdot C_3H_7COOC_4H_9$ 4.46 and $TiCl_4 \cdot C_3H_7COOC_5H_{11}$ 4.37 D. As we see, all three complex compounds have very similar dipole moments.

Complex compounds of tin tetrachloride. Unlike the titanium compounds, the complex compounds of $SnCl_4$ with the same esters are liquid at room temperature and show a great tendency to undercooling. The data of Tables 4-6 characterize the dependence of the dielectric permeability, density and polarization of the tin complexes on their concentration in benzene.

We determined the electronic polarization from data for the refraction of the complex compounds; the respective values are 95.56, 112.42 and 119.20 cc.

In the case of the tin complexes we calculated the electronic polarization as the sum of the molar refractions of the components of the complex. We took the refraction of the Sn-Cl bond from the literature [11]. The experimental data were found to be somewhat lower than the calculated ones; this is due to deformation of the atoms entering the complex compound during formation of the latter from the components. The difference between the calculated and the experimental value is evidently greater the more strongly the atoms are deformed during formation of the complex.

TABLE 1
The Complex $TiCl_4 \cdot C_3H_7COOC_2H_5$ in Benzene
P_∞ = 500 cm³, R = 66.52 cm³

C	ε	d	P_2
0.0109	2.5832	0.8925	444
0.0155	2.6830	0.8986	428
0.0200	2.7828	0.9050	393
0.0251	2.8710	0.9110	373
0.0300	2.9692	0.9187	360

TABLE 2
The Complex $TiCl_4 \cdot C_3H_7COOC_4H_9$ in Benzene
P_∞ = 499 cm³, R = 75.89 cm³

C	ε	d	P_2
0.0052	2.4278	0.8852	473
0.0086	2.5094	0.8893	454
0.0116	2.5838	0.8941	442
0.0201	2.7798	0.9041	410
0.0560	3.3587	0.9482	320
0.0660	3.5202	0.9599	309

TABLE 3
The Complex $TiCl_4 \cdot C_3H_7COOC_5H_{11}$ in Benzene
P_∞ = 496 cm³, R = 81.55 cm³

C	ε	d	P_2
0.0075	2.4764	0.8864	460
0.0151	2.5880	0.8941	431
0.0290	2.8984	0.9061	386
0.0309	2.9598	0.9089	382
0.0427	3.1189	0.9203	355
0.0614	3.3411	0.9338	322

TABLE 4
The Complex $SnCl_4 \cdot 2C_3H_7COOC_2H_5$ in Benzene
P_∞ = 988 cm³, R = 95.56 cm³

C	ε	d	P_2
0.0075	2.7114	0.8897	901
0.0102	2.8580	0.8942	866
0.0149	3.0617	0.9026	817
0.0200	3.3618	0.9090	787
0.0308	4.0409	0.9241	779

TABLE 5
The Complex $SnCl_4 \cdot 2C_3H_7COOC_4H_9$ in Benzene
P_∞ = 984 cm³, R = 112.42 cm³

C	ε	d	P_2
0.0065	2.6502	0.8900	924
0.0080	2.7439	0.8941	911
0.0190	3.4199	0.9102	864
0.0260	3.7128	0.9196	806
0.0385	4.5004	0.9468	748

TABLE 6
The Complex $SnCl_4 \cdot 2C_3H_7COOC_5H_{11}$ in Benzene
P_∞ = 976 cm³, R = 119.20 cm³

C	ε	d	P_2
0.0075	2.7552	0.8909	918
0.0098	2.8423	0.8959	910
0.0144	3.1081	0.9052	879
0.0176	3.3012	0.9098	869
0.0320	4.1687	0.9351	812

For the first complex we obtained a dipole moment of 6.52; for the second 6.44, and for the third 6.38 D. We see that the three values are very similar.

In Table 7 are set forth the values of the dipole moments (μ) of the complexes that we investigated, together with the literature values of the dipole moments of some other complex compounds of $TiCl_4$ and $SnCl_4$ [12].

Table 7 also gives the dipole moments of the corresponding organic molecules present in the complexes. The last column shows the increase in dipole moment due to complex formation in the form of difference between the dipole moments of the complex and the polar component.

For complex compounds of the type of $TiCl_4 \cdot A$ or $SnCl_4 \cdot A$ (where A is the organic molecule entering into the composition of the complex), the rise in the moment ($\Delta\mu$) was calculated as the difference $\mu - \mu_1$, while for compounds with the formula $SnCl_4 \cdot 2A$, calculation was based upon the formula $\mu - \mu_1\sqrt{2}$, the assumption being made that two molecules of the organic addend are arranged toward each other in the complex at an angle of 90°.

We see from the data cited (Table 7) that interaction of halides of titanium and tin with various organic compounds leads to formation of complex molecules with a high polarity. The very large rise in the dipole moment of the complex compound in comparison with the moment of the molecule of the polar component

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TABLE 7

Compound	μ	μ_1	$\mu - \mu_1$ or $\mu - \mu_1 \sqrt{2}$
$TiCl_4 \cdot C_2H_5CN$	6.05	3.57—3.66	2.48—2.39
$TiCl_4 \cdot C_6H_5CN$	6.16	3.90	2.26
$TiCl_4 \cdot C_3H_7COOC_2H_5$	4.52	1.74	2.78
$TiCl_4 \cdot C_3H_7COOC_4H_9$	4.46	1.70	2.76
$TiCl_4 \cdot C_3H_7COOC_5H_{11}$	4.37	1.73	2.64
$SnCl_4 \cdot C_6H_5CN$	7.06—6.55	3.90	3.16—2.65
$SnCl_4 \cdot (C_2H_5)_2O$	3.60	1.14	2.46
$SnCl_4 \cdot 2(CH_3)_2CO$	7.70	2.72	3.90
$SnCl_4 \cdot 2CH_3COC_6H_5$	8.70	2.97	4.50
$SnCl_4 \cdot 2C_6H_5CHO$	7.5—8.1	2.80	3.57—4.13
$SnCl_4 \cdot 2C_3H_7COOC_2H_5$	6.52	1.74	4.05
$SnCl_4 \cdot 2C_3H_7COOC_4H_9$	6.44	1.70	4.03
$SnCl_4 \cdot 2C_3H_7COOC_5H_{11}$	6.38	1.73	3.92

cannot be explained merely as a phenomenon of polarized interaction; it testifies to a profound chemical interaction between the components with formation of a new bond. Since, according to the data of a number of authors [13-16], the dipole moments of titanium and tin tetrachlorides are zero, the differences between the moments of the complex compound and of the polar component must be attributed to the development of a new bond during complex formation (the donor-acceptor bond); this is accompanied by development of a new covalent bond with a high degree of polarization.

A conspicuous feature is the constancy of the rise of dipole moments of the complex compounds of titanium and tin chlorides with ethyl, isobutyl and isoamyl esters of butyric acid that we investigated.

This constancy is evidence of the identical stabilities of the investigated complexes; it also suggests that the size of the alcohol radical in the ester scarcely influences the stability of the complex. Confirmatory evidence is provided by some literature data and our own data on physico-chemical investigations of similar systems. N. S. Kurnakov and N. K. Voskresenskaya [5] compared the heats of mixing of $SnBr_4$ with ethyl formate and ethyl acetate on the one hand with the heats of mixing of $SnBr_4$ with isobutyl formate and isobuty acetate on the other hand, and arrived at the conclusion that replacement of one alcohol radical by another is scarcely reflected in the curve of heats of mixing.

We observed a similar phenomenon in the investigation of the heats of mixing of titanium tetrachloride with ethyl acetate, propyl acetate and n-butyl acetate [17, 18].

Replacement in an ester of one alcohol radical by another likewise has little influence upon the magnitude of the internal friction of the complex compound [10]. Thus, for example, the complex compounds of $SnCl_4$ that we investigated have the following values of internal friction at 30° (in centipoises): $SnCl_4 \cdot 2C_3H_7COOC_2H_5$ 16.55, $SnCl_4 \cdot 2C_3H_7COOC_4H_9$ 15.94 and $SnCl_4 \cdot 2C_3H_7COOC_5H_{11}$ 15.80. We also observed a similar picture in the case of titanium complexes.

However, as we have already pointed out above, increase in size of the alcoholic radical in the ester leads to a considerable fall in melting point. This may be a consequence of the screening effect of the nonpolar hydrocarbon radical. It must also be remembered that increase in size of the acidic radical in the ester results in a sharp fall in the coefficient of internal friction of the complex and of its thermal effect. Thus, for example, in the series of complex compounds: $SnCl_4 \cdot 2HCOOC_2H_5$, $SnCl_4 \cdot 2CH_3COOCH_2H_5$ and $SnCl_4 \cdot 2C_3H_7COOC_2H_5$, the viscosity at 25° falls from 71.97 to 19.31 centipoises [5]. We may also note that the dipole moment of the complex compound $SnCl_4 \cdot 2CH_3COOC_2H_5$ is higher (7.3 D) [19] than the moment of $SnCl_4 \cdot 2C_3H_7COOC_2H_5$ (6.52 D).

From what has been said, we can conclude that the degree of stability of the ester complexes of titanium and tin is governed not only by the size of the hydrocarbon radical but also by its position in the ester. This in turn leads to the hypothesis that the active factor that characterizes complex formation is probably the oxygen of the carboxyl group in the ester [5]. However, this aspect calls for supplementary research.

Inspection of the data of Table 7 reveals that complex compounds with the composition $SnCl_4 \cdot 2A$, in which the bond between tin tetrachloride and the organic compound is effected through oxygen, have approximately identical increases of dipole moment with a mean value of 4 D. In the case of complex compounds of $SnCl_4$ and $TiCl_4$ with organic oxygen-containing substances of equimolar composition, the difference $\mu - \mu_1$, has a relatively constant value (2.5-2.6 D). This constancy of rise of dipole moment during complex formation is evidence of similarity of structure of the complex compounds in question.

The deviation of the increment of dipole moments from the mean value in some complex compounds may be explained by their differing degree of stability in solution. This is clearly seen with the complex compounds formed by $TiCl_4$ and $SnCl_4$ with benzonitrile.

The constancy of the difference between the dipole moment of the complex and the oxygen-containing addend in complex compounds of the type of $TiCl_4 \cdot A$ or $SnCl_4 \cdot A$ is evidence of their identical structures. Judging by the results of measurements of dipole moments, the complexes of tin tetrachloride with the above-enumerated esters that we investigated possess a cis-structure.

SUMMARY

1. The dipole moments of some complex compounds of titanium and tin tetrachlorides were investigated: $TiCl_4 \cdot C_3H_7COOC_2H_5$ (4.52 D), $TiCl_4 \cdot C_3H_7COOC_4H_9$ (4.46 D), $TiCl_4 \cdot C_3H_7COOC_5H_{11}$ (4.37 D), $SnCl_4 \cdot 2C_3H_7COOC_2H_5$ (6.52 D), $SnCl_4 \cdot 2C_3H_7COOC_4H_9$ (6.44 D), $SnCl_4 \cdot 2C_3H_7COOC_5H_{11}$ (6.38 D).

2. Formation of complex compounds of $SnCl_4$ and $TiCl_4$ with esters of mono-basic acids leads to a marked increase in polarization, as reflected in the higher values of the dipole moments.

3. The difference between the dipole moments of the complex and the ester, both in the case of 1 : 1 compounds and 1 : 2 compounds, is relatively small and substantially independent of the length of the alcohol radical. The difference is 2.5-2.6 D in the case of titanium complexes and about 4 D in that of tin complexes.

4. It is established that complex compounds formed by $TiCl_4$ and $SnCl_4$ with one molecule of oxygen-containing compound must have nearly identical structures.

5. On the basis of measurements of dipole moments it is shown that complex compounds of tin tetrachloride with two molecules of ester must have a cis-structure.

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THE TERNARY RECIPROCAL SYSTEM OF THE CHLORIDES AND SULFATES OF POTASSIUM AND CALCIUM

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Investigation of the surface of crystallization of the system, K, Ca || Cl, SO_4 is part of a larger scheme of study of the formation in fused salts of heteroionic complexes, i.e. of salts consisting of four different ions.

Anhydrokainite $MgSO_4 \cdot KCL$ [1] may be regarded as the classic example of such complexes. With the objective of establishing the possibility of formation of analogous salts when magnesium sulfate was replaced by calcium sulfate, we also made a study, by the visual-polythermal fusion method, of the surface of crystallization of the reciprocal system of the chlorides and sulfates of potassium and calcium which had formerly been studied [2] by the method of plotting of cooling curves.

According to the data of [2], the reciprocal system is deficient in internal fields. Compounds exist only on the sides of the $K_2SO_4 \cdot 2CaSO_4$ square (calcium langbeinite) and of the $CaCl_2 \cdot KCl$ square (calcium carnallite) (Fig. 1).

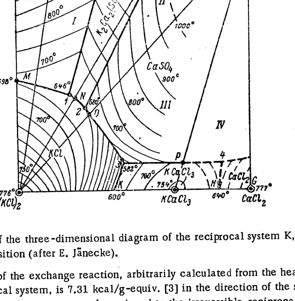

Fig. 1. Projection of the three-dimensional diagram of the reciprocal system K, Ca || Cl, SO_4 on the square of composition (after E. Jänecke).

The thermal effect of the exchange reaction, arbitrarily calculated from the heats of formation of the components of the reciprocal system, is 7.31 kcal/g-equiv. [3] in the direction of the stable pair $CaSO_4$-KCl. In the classification of [4, 5] the system must be assigned to the irreversible-reciprocal type.

EXPERIMENTAL*

Binary systems. 1. K_2SO_4-$CaSO_4$ (Fig. 3). According to the data of [4] the diagram comprises 4 branches: potassium sulfate, the α- and β-forms of calcium langbeinite $K_2SO_4 \cdot 2CaSO_4$ (with a transition point at 936°) and calcium sulfate.

The data of S. M. Miukimov, N. I. Krylova and A. G. Bergman [7] agree with those of Müller [6], but the interpretations of the whole diagram are quite different in the two papers. The existence was established [7], in a study of the ternary system of the sulfates of potassium, magnesium and calcium, of not one but of two compounds (melting with decomposition) with the suggested compositions: $K_2SO_4 \cdot 2CaSO_4$ and $K_2SO_4 \cdot 3CaSO_4$.

In a study of a series of internal cuts, we repeated the individual points of the system and obtained data similar to those in [6]; the difference in the individual points of the composition did not exceed 2-4°.

Study of the system K, Ca ‖ Cl, SO_4 revealed the existence of two independent compounds, but we did not detect the polymorphic difference in the case of $K_2SO_4 \cdot 2CaSO_4$ which was found by Müller [6]. The compound $K_2SO_4 \cdot 2CaSO_4$ agrees with these data, but the composition of the second, $2K_2SO_4 \cdot 3CaSO_4$, found on the basis of projection of the curves of common crystallization and of triangulation of the reciprocal system, does not agree with the composition which was established in [7] as $K_2SO_4 \cdot 3CaSO_4$.

Fig. 2. Projection of the three-dimensional diagram of the reciprocal system K, Ca ‖ Cl, SO_4 on the square of composition (from our data).

2. $CaCl_2$-K_2Cl_2 (Fig. 3) [8, 9]. A compound $CaCl_2 \cdot KCl$, m.p. 745°, exists. According to our data there are eutectic points at 635° and 86% and 597 and 40% $CaCl_2$**.

3. $CaCl_2$-$CaSO_4$ (Fig. 3) [10]. Repeated by us. It is a system with a eutectic at 708° and 12.5% $CaSO_4$.

4. K_2Cl_2-K_2SO_4 [11] (Fig. 3). Repeated by us. A system with a eutectic at 698° and 43% K_2SO_4.

Diagonal Cuts

Stable cut K_2Cl_2-$CaSO_4$ (Table 1, Fig. 3). This has been studied [10] from 0 to 46.3% calcium sulfate,

* A platinum crucible was used; the thermocouple was Pt, Pd, Au/Pt, Rh.

** In all cases the composition of the mixtures is given in equimolar percentages.

Fig. 3. Sides and diagonal cuts of the reciprocal system K, Ca ‖ Cl, SO_4. $K_2SO_4 \cdot 2CaSO_4$ — A, $2K_2SO_4 \cdot 3CaSO_4$ — B.

and the existence of a eutectic at 685° and 31.8% $CaSO_4$ was established between potassium chloride and a compound with the suggested composition $CaSO_4 \cdot KCl$, i.e. calcium anhydrokainite.

We detected three branches in the interval of 0 to 60% calcium sulfate: potassium chloride, calcium sulfate and a compound that we called X, melting with decomposition at 790° and 44.5% $CaSO_4$. The eutectic point N_I, situated at 688° and 32% calcium sulfate, and the point of incongruent melting N_{II} at 790° have the character of turning points (Figs. 2 and 4). This indicates that a peak of the internal compound must exist on the stable diagonal, i.e. it is a double heterosalt. The proposed composition of Compound X was established on the basis of the temperatures of complete solidification of Melts 1 and 2 of Cuts XIII and XV (Table 3) and of triangulation of the reciprocal system.

The unstable diagonal cut of $CaCl_2$-K_2SO_4 (Table 2, Fig. 3). It passes through five fields: calcium chloride, calcium sulfate, two binary sulfates of potassium and calcium formed in the system K_2SO_4-$CaSO_4$, and a branch of potassium sulfate, intersecting at 645° and 10%, 785° and 57.5%, 770° and 65%, 720° and 73.5% potassium sulfate.

Internal cuts (Fig. 4)*. 23 internal cuts were studied. Data for the 1st series of Cuts I-VII appear in Tables 3 and 4 and are plotted in Fig. 5. The boundaries of the fields of calcium chloride and $CaCl_2 \cdot KCl$ enclose the lower wedge-shaped internal field of the double heterosalt X; the existence of two ternary eutectic points was established: E_3 at 580° and E_4 at 604°.

2nd series of Cuts IX-XI (Tables 3 and 4, Fig. 6). The occurrence of two ternary eutectic points E_1 at 644° and E_2 at 675° was established from the temperatures of complete solidification of the melts of the cuts of the 2nd series and from the projection of the curves of common crystallization (Fig. 8).

* Only a portion of the experimental data is presented in the tables.

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TABLE 1

$K_2Cl_2 - CaSO_4$ Diagonal Cut

% $CaSO_4$	Temperature	% $CaSO_4$	Temperature	% $CaSO_4$	Temperature	% $CaSO_4$	Temperature
0	775°	32.5	696°	40	770°	48	836
20	722	34	716	42	786	50	846
25	708	36	736	44	790	55	896
30	694	37.5	752	46	820	—	—

TABLE 2

Diagonal Cut $CaCl_2$- K_2SO_4

% K_2SO_4	Temperature	% K_2SO_4	Temperature	% K_2SO_4	Temperature	% K_2SO_4	Temperature
0	772°	25	850°	50	846°	67.5	764°
5	710	30	890	55	808	70	750
7.5	680	35	906	57.5	785	72.5	732
10	655	37.5	910	60	782	75	740
15	740	40	904	62.5	780	80	848
20	805	45	886	65	770	85	920
						90	975

* All the tables in the present paper give the equimolar percentages of the added component and the temperature of appearance of the first crystals.

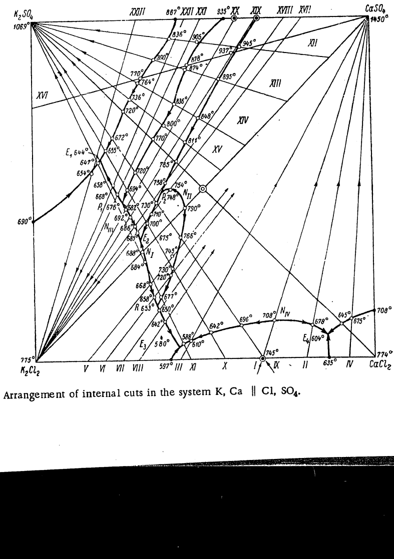

Fig. 4. Arrangement of internal cuts in the system K, Ca ‖ Cl, SO_4.

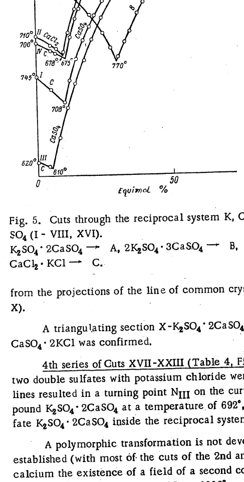

Fig. 5. Cuts through the reciprocal system K, Ca ‖ Cl_2, SO_4 (I - VIII, XVI).
$K_2SO_4 \cdot 2CaSO_4 \rightarrow$ A, $2K_2SO_4 \cdot 3CaSO_4 \rightarrow$ B,
$CaCl_2 \cdot KCl \rightarrow$ C.

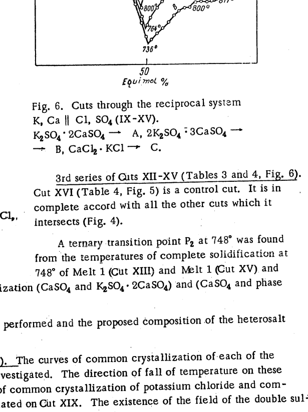

Fig. 6. Cuts through the reciprocal system K, Ca ‖ Cl, SO_4 (IX-XV).
$K_2SO_4 \cdot 2CaSO_4 \rightarrow$ A, $2K_2SO_4 \cdot 3CaSO_4 \rightarrow$
$\rightarrow$ B, $CaCl_2 \cdot KCl \rightarrow$ C.

3rd series of Cuts XII-XV (Tables 3 and 4, Fig. 6). Cut XVI (Table 4, Fig. 5) is a control cut. It is in complete accord with all the other cuts which it intersects (Fig. 4).

A ternary transition point P_2 at 748° was found from the temperatures of complete solidification at 748° of Melt 1 (Cut XIII) and Melt 1 (Cut XV) and from the projections of the line of common crystallization ($CaSO_4$ and $K_2SO_4 \cdot 2CaSO_4$) and ($CaSO_4$ and phase X).

A triangulating section X-$K_2SO_4 \cdot 2CaSO_4$ was performed and the proposed composition of the heterosalt $CaSO_4 \cdot 2KCl$ was confirmed.

4th series of Cuts XVII-XXIII (Table 4, Fig. 7). The curves of common crystallization of each of the two double sulfates with potassium chloride were investigated. The direction of fall of temperature on these lines resulted in a turning point N_{III} on the curves of common crystallization of potassium chloride and compound $K_2SO_4 \cdot 2CaSO_4$ at a temperature of 692°, situated on Cut XIX. The existence of the field of the double sulfate $K_2SO_4 \cdot 2CaSO_4$ inside the reciprocal system was confirmed.

A polymorphic transformation is not developed in $K_2SO_4 \cdot 2CaSO_4$ in the cuts examined, but instead we established (with most of the cuts of the 2nd and 3rd series) in the binary system of sulfates of potassium and calcium the existence of a field of a second compound whose peak had to be situated between the melting point of compound $K_2SO_4 \cdot 2CaSO_4$ at 1006° and 66.6% potassium sulfate and the point of incongruent melting of this compound at 935° and 57% calcium sulfate. Within these limits the most probable compound is one with 60% calcium sulfate, i.e. the compound $2K_2SO_4 \cdot 3CaSO_4$.

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TABLE 3
Internal Cuts of the ystem K, Ca || Cl, SO_4

Cut *I* % $CaSO_4$	Cut *I* Temperature	Cut *V*** % $CaSO_4$	Cut *V*** Temperature	Cut *IX* % $CaSO_4$	Cut *IX* Temperature	Cut *XV***** % K_2SO_4	Cut *XV***** Temperature
0	745°	0	735°	44	750°	0	894°
5	724	8	710	50	732	7.5	874
10	708	16	686	54	730	12	852
12.5	740	20	676	56	720	16	832
15	770	22	668	58	714	18	816
20	820	24	714	60	704	20	811
25	854	26	732	64	680	25	811
30	890	28	740	66	680	30	800
35	925	30	745	68	710	32.5	800
		32	764	72	764	35	796
		36	800	76	820	40	775
		40	830	82	906	45	756
		44	860			47.5	746
		48	900			50	750
						55	808
						60	862

Cut *II** % $CaSO_4$	Cut *II** Temperature	Cut *IX* % K_2SO_4	Cut *IX* Temperature	Cut *XIII**** % K_2SO_4	Cut *XIII**** Temperature
0	700°	0	745°	20	958°
5	690	4	722	22.5	940
7	686	6	710	25	920
10	686	8	700	27.5	900
12.5	715	10	700	30	894
19	800	12	720	32.5	894
24	850	16	760	35	892
30	894	20	785	37.5	885
40	970	24	795	40	874
		28	797	42.5	872
		30	790	45	860
		34	774	47.5	848
		36	768	50	836
		38	772	52.6	800
		40	770	55	822
		42	760	60	852

* Melts of Cut II solidify at 604°.
** Melts of Cut V solidify at 580°.
*** Melt 1 of Cut V solidifies at 748°, Melt 2 of Cut XIII solidifies at 675°.
**** Melt 1 of Cut XV solidifies at 748°, Melt 2 of Cut XV solidifies at 675°.

The surface of the system K, Ca || XCl, SO_4 is divided into 8 fields, three of which belong to compounds of the sides while one field is formed on the stable diagonal of the reciprocal system of the proposed composition $CaSO_4 \cdot 2KCl$. A compound with a similar formula $CaSO_4 \cdot 2KCl \cdot 1/2\,H_2O$ was previously detected in aqueous solution [12].

We found one of the compounds of the side of the square with the composition $2K_2SO_4 \cdot 3CaSO_4$ for the first time from the situation of its field of crystallization inside the reciporcal system.

The projection on the side of the square of K_2SO_4-K_2Cl_2 (Fig. 8) reveals a regular fall of temperature and complete correspondence in the location of the curves of common crystallization and the multiple points.

TABLE 4 (Summary)
Internal Cuts of the System K, Ca || Cl, SO_4

Series number	Cut number	Composition of original mixture of components	Melting point of original mixture	Added component	Branch I	Intersection a*	Intersection temperature	Branch II	Intersection a*	Intersection temperature	Branch III	Intersection a*	Intersection temperature	Branch IV	Intersection a*	Intersection temperature	Branch V	Intersection a*	Intersection temperature	Branch VI
1	*I*	33.33% K_2Cl_2 + 66.67% $CaCl_2$	745°	$CaSO_4$	*C*	10	708°	$CaSO_4$												
1	*II*	20% K_2Cl_2 + 80% $CaCl_2$	710	$CaSO_4$	*C*	9	678	$CaSO_4$												
1	*III*	57.5% K_2Cl_2 + 42.5% $CaCl_2$	620	$CaSO_4$	*C*	5	610	$CaSO_4$												
1	*IV*	92.5% $CaCl_2$ + 7.5% K_2Cl_2	700	$CaSO_4$	$CaCl_2$	11	675	$CaSO_4$												
1	*V*	15% $CaCl_2$ + 85% K_2Cl_2	735	$CaSO_4$	KCl	22	668	*X*	30	745°	$CaSO_4$									
1	*VI*	20% $CaCl_2$ + 80% K_2Cl_2	720	$CaSO_4$	KCl	18	658	*X*	25	720	$CaSO_4$									
1	*VII*	25% $CaCl_2$ + 75% K_2Cl_2	695	$CaSO_4$	KCl	14	650	$CaSO_4$												
1	*VIII*	30% $CaCl_2$ + 70% K_2Cl_2	670	$CaSO_4$	KCl	11	642	$CaSO_4$												
2	*IX*	33.33% K_2Cl_2 + 66.67% $CaCl_2$	745	K_2SO_4	*C*	9	696	$CaSO_4$	36.5	766	*X*	46.6	730°	*A*	56	720°	*B*	65	672	K_2SO_4
2	*X*	45% K_2Cl_2 + 55% $CaCl_2$	708	K_2SO_4	*C*	7.5	642	$CaSO_4$	26.5	730	*X*	40	700	*A*	50	694	*B*	62	655	K_2SO_4
2	*XI*	55% K_2Cl_2 + 45% $CaCl_2$	640	K_2SO_4	*C*	5	588	$CaSO_4$	18.5	677	*X*	28.5	684	KCl	59	647	K_2SO_4			
3	*XII*	12.5% K_2Cl_2 + 87.5% $CaSO_4$	1240	K_2SO_4	$CaSO_4$	30	945	*A*	45	905	*B*	54	836	K_2SO_4						
3	*XIII*	25% K_2Cl_2 + 75% $CaSO_4$	1095	K_2SO_4	$CaSO_4$	27	895	*A*	40	874	*B*	52.5	800	K_2SO_4						
3	*XIV*	37.5% K_2Cl_2 + 62.5% $CaSO_4$	960	K_2SO_4	$CaSO_4$	22.5	848	*A*	33	836	*B*	50 5	764	K_2SO_4						
3	*XV*	45% K_2Cl_2 + 55% $CaSO_4$	894	K_2SO_4	$CaSO_4$	18.5	811	*A*	30	800	*B*	49	736	K_2SO_4						
Control	*XVI*	25% K_2Cl_2 + 75% K_2SO_4	900	$CaSO_4$	K_2SO_4	30	770	*B*	45	878	*A*	57.5	937	$CaSO_4$						
4	*XVII*	20% K_2SO_4 + 80% $CaSO_4$	Not determined	K_2Cl_2	$CaSO_4$	50	754	*X*	57.5	710	*A*	62.5	685	KCl						
4	*XVIII*	25% K_2SO_4 + 75% $CaSO_4$		K_2Cl_2	$CaSO_4$	60.5	758	*A*	67.5	688	KCl									
4	*XIX*	33.33% K_2SO_4 + 66.67% $CaSO_4$	1006	K_2Cl_2	*A*	58	692	KCl												
4	*XX*	40% K_2SO_4 + 60% $CaSO_4$	982	K_2Cl_2	*A*	57	682	KCl												
4	*XXI*	50% K_2SO_4 + 50% $CaSO_4$	920	K_2Cl_2	*B*	51	668	KCl												
4	*XXII*	55% K_2SO_4 + 45% $CaSO_4$	890	K_2Cl_2	*B*	49	658	KCl												
4	*XXIII*	70% K_2SO_4 + 30% $CaSO_4$	955	K_2Cl_2	K_2SO_4	45	654	KCl												

Notes: One asterisk denotes equimolar percentages of added components, two asterisks denote the temperature of appearance of the first crystals; the following symbols are used here and in Table 5: A — $K_2SO_4 \cdot 2CaSO_4$, B — $2K_2SO_4 \cdot 3CaSO_4$, C — $CaCl_2 \cdot KCl$, X — $CaSO_4 \cdot 2KCl$.

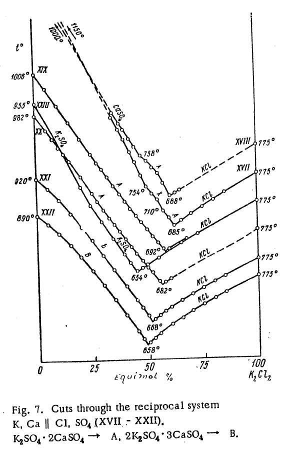

Fig. 7. Cuts through the reciprocal system K, Ca ‖ Cl, SO_4 (XVII - XXII). $K_2SO_4 \cdot 2CaSO_4 \rightarrow$ A, $2K_2SO_4 \cdot 3CaSO_4 \rightarrow$ B.

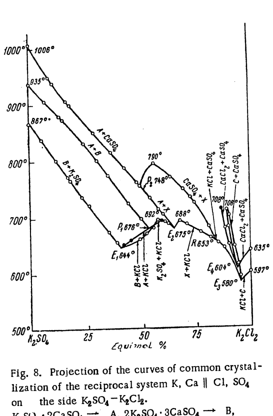

Fig. 8. Projection of the curves of common crystallization of the reciprocal system K, Ca ‖ Cl, SO_4 on the side $K_2SO_4 - K_2Cl_2$. $K_2SO_4 \cdot 2CaSO_4 \rightarrow$ A, $2K_2SO_4 \cdot 3CaSO_4 \rightarrow$ B, $CaCl_2 \cdot KCl \rightarrow$ C, $KCl \cdot CaSO_4 \rightarrow$ X.

TABLE 5

Compositions of invariant points of the system K, Ca ‖ Cl, SO_4

Item number	Names of invariant points		Temperature	Composition (in mol.-%)				Equilibrium solid phases
				$CaSO_4$	K_2Cl_2	K_2SO_4	$CaCl_2$	
1	Eutectics	E_1	644°	19	41	40	—	K_2SO_4 + B + KCl
2		E_2	675	30	66	5	—	A + X + KCl
3		E_3	580	4	58	—	38	KCl + $CaSO_4$ + C
4		E_4	604	6.5	14	—	79.5	$CaSO_4$ + $CaCl_2$ + C
5	Transition points	P_1	676	26	54	20	—	A + B + KCl
6		P_2	748	37.5	51	11.5	—	$CaSO_4$ + X + A
7	Peritectic	R	653	16	65	—	19	X + KCl + $CaSO_4$

We found four ternary eutectic points E_1 at 644°, E_2 at 675°, E_3 at 580° and E_4 at 604°, and one transition point P_2 at 748° from the temperature of complete solidification of the melts of the internal cuts. These were confirmed by the intersections of the curves of common crystallization. A ternary transition point P_1 at 676° and a peritectic point R at 653° were found on the basis of the projections on the sides of the square.

The system contains 3 stable sections: one diagonal and two adiagonals; they divide the reciprocal system into 4 independent ternary systems (Fig. 2):

1) $CaCl_2$, $CaSO_4$, $CaCl_2 \cdot KCl$ (designated by IV');

2) $CaCl_2 \cdot KCl$, $CaSO_4$, K_2Cl_2 (designated by III');

3) $CaSO_4$, K_2Cl_2, $K_2SO_4 \cdot 2CaSO_4$;

4) $K_2SO_4 \cdot 2CaSO_4$, K_2Cl_2, K_2SO_4.

The presence of the peak of Compound X on the diagonal K_2Cl_2-$CaSO_4$ results in a second triangulation of the third system by the unstable section X-$K_2SO_4 \cdot 2CaSO_4$ into two phase triangles: 1) $CaSO_4 \cdot 2CaSO_4$ (designated V') and 2) $K_2SO_4 \cdot 2CaSO_4$, X, K_2Cl_2 (designated II'). But the existence of a second compound, melting with decomposition, in the system of the sulfates of potassium and calcium, leads to the development of an unstable triangulating section of $2CaSO_4 \cdot 3CaSO_4$-K_2Cl_2 which divides the fourth ternary system into two phase triangles: 1) $K_2SO_4 \cdot 2CaSO_4$, K_2Cl_2, $2K_2SO_4 \cdot 3CaSO_4$ (designated VI') and 2) $2K_2SO_4 \cdot 3CaSO_4$, K_2Cl_2, K_2SO_4 (designated I').

The triangulating section X-$K_2SO_4 \cdot 2CaSO_4$ was carried out by us on the basis of the temperature of complete solidification of the melts of Cuts XIII (Melt 1) and XV (Melt 1) at 748°, whereas the adjacent Melts 2 of these cuts solidified at 675° (Table 3). It follows from this that the latter are in another phase triangle and the triangulating section must pass between the points of compositions corresponding to the specified melts. On joining the peak of $K_2SO_4 \cdot 2CaSO_4$ with the middle of the stable diagonal section by a straight line, we obtained this section and the two phase triangles V' and II' with the temperatures of complete solidification stated above.

The reciprocal system K, Ca ‖ Cl, SO_4 has been investigated in aqueous solution at 25° [13]; water has a great influence upon the structure of the system. The enormous gypsum field occupies nearly the whole area of the square of the isotherm of the system. The only double salt formed is syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, whereas in melts a large number of complexes of salts are formed which are susceptible to hydration, such as calcium chloride and calcium sulfate.

SUMMARY

1. The surface of crystallization of the reciprocal system of the chlorides and sulfates of potassium and calcium consists of eight fields meeting at seven triple points. The data obtained differ in important respects from those of Jänecke [2] who did not detect two fields of compounds: the double sulfate $2K_2SO_4 \cdot 3CaSO_4$ and the double heterosalt $CaSO_4 \cdot 2KCl$ on the stable diagonal.

Two transition points (P_1 at 676° and P_2 at 748°) and one point R at 653° were found.

2. A comparison of the two diagrams of the reciprocal system in aqueous solution and in a melt indicates weakening of the reaction of complex formation in aqueous solution under the influence of the aggressive action of water.

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COMPLEX FORMATION AND DOUBLE DECOMPOSITION IN THE RECIPROCAL SYSTEM OF THE FLUORIDES AND SULFATES OF LEAD AND POTASSIUM

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The purpose of investigation of the systems K, Pb || F, SO_4 was to elucidate the behavior of compounds developed on the $K_2F_2 \cdot 2K_2SO_4$ and $K_2SO_4 \cdot 2PbSO_4$ sides and to establish the type of the system. The thermal effect of the double decomposition was 6.84 kcal in the direction of the components PbF_2 and K_2SO_4. On the two contiguous sides of the square are situated the compounds (melting without decomposition) $K_2F_2 \cdot 2K_2SO_4$ at 880° and $K_2SO_4 \cdot 2PbSO_4$ at 946°; the remaining two sides of the square are simple eutectic systems.

EXPERIMENTAL

Procedure. The investigation was carried out by the visual-polythermal fusion method. The crucible and stirrer were of platinum. The thermocouple was Au, Pt, Pd/Pt, Rh. A 40 mV millivoltmeter was used. All calculations are expressed in mol.-%. For economy of space, a portion of the cuts and experimental points is omitted.

Lead fluoride was prepared by interaction of twice-distilled hydrofluoric acid with chemically pure lead carbonate. The potassium fluoride was a chemically pure grade which was previously dehydrated.

The potassium sulfate was a twice-recrystallized chemically pure grade. Lead sulfate was prepared by precipitation of lead nitrate with pure sulfuric acid. Melting points of salts: PbF_2 826°, KF 850°, K_2SO_4 1074°, $PbSO_4$ 1100°.

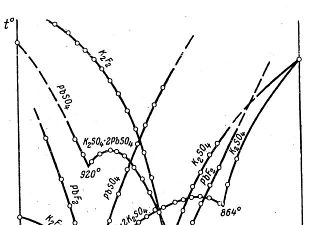

Fig. 1. Fusibility diagram of the binary systems. Explanation in text.

Fig. 2. Diagonal sections of the reciprocal system.

Binary systems. 1. $K_2F_2-K_2SO_4$ (Fig. 1). This has previously been investigated [1, 2]. We confirmed the existence of the compound $K_2F_2 \cdot 2K_2SO_4$ but with a slightly different melting point (880°) and eutectic points E_1 783° and 27% K_2SO_4; E_2 864°, 73.5% K_2SO_4.

2. $K_2SO_4-PbSO_4$ (Fig. 1). This has previously been studied [3, 4]. Our data confirm the existence of the double compound $K_2SO_4 \cdot 2PbSO_4$, melting without decomposition at 946°. Eutectic points are E_1 805° and 45% $PbSO_4$, E_2 920° and 75% $PbSO_4$. Data in [3,4]: melting point of compound 948°, but eutectics E_1 792° and 45% $PbSO_4$, E_2 837° and 81% $PbSO_4$; the compound $K_2SO_4 \cdot PbSO_4$ appeared in the solidus at 619°; we plotted the cooling curve of the 1 : 1 melt and obtained a characteristic halt at 628°.

3. $K_2F_2-PbF_2$ (Fig. 1). Eutectic point at 460° and 57.5% PbF_2. It was investigated by us.

4. PbF_2-PbSO_4 (Fig. 1). This was studied by us. The fusion curve comprises two steeply descending branches of the components. Eutectic point at 520° and 26.5% $PbSO_4$.

Diagonal cuts. 1. Stable diagonal of $PbF_2-K_2SO_4$ (Fig. 2, Table 1). Consists of two branches of the components which intersect at a eutectic point at 480° and 22.5% K_2SO_4.

2. Unstable diagonal of $K_2F_2-PbSO_4$ (Fig. 2, Table 1). Consists of six intersecting branches.

TABLE 1

Binary Systems and Diagonal Cuts

$K_2F_2-PbF_2$		PbF_2-PbSO_4		$PbF_2-K_2SO_4$		$K_2F_2-PbSO_4$			
% PbF_2	Temp.	% $PbSO_4$	Temp.	% K_2SO_4	Temp.	% $PbSO_4$	Temp.	% $PbSO_4$	Temp.
15	816°	10	728°	10	660°	10	822°	50	756°
20	803	15	668	16	575	15	782	53	731
26	778	18	630	20	520	20	754	56	711
29	766	20	605	22	486	23	769	59	672
35	736	23	571	25	500	26	782	62	632
41	682	25	542	28	530	29	785	65	611
47	632	30	571	34	590	32	777	68	623
53	546	35	637	40	652	35	762	71	672
56	486	40	687	43	682	38	752	74	711
59	480	43	718	46	714	41	762	77	752
62	504	46	746	49	744	44	770	80	812
65	530	49	775	52	775	47	769	82	860
71	584	52	800	55	800				
74	610	55	824	58	826				
Intersection 460°, 57.5% PbF_2.		Intersection 520°, 26.5% $PbSO_4$.		Intersection 480°, 22.5% K_2SO_4.		Intersection 744°, 18% $PbSO_4$; 747°, 37% $PbSO_4$; 623°, 68% $PbSO_4$; 604°, 63.5% $PbSO_4$; 764°, 78.5% $PbSO_4$.			

The Ternary Reciprocal System

The joint presence of four binary systems and two diagonal and 19 internal cuts (Fig. 3) offers the possibility of determining the liquidus surface of the system which comprises 7 fields of crystallization; 4 fields belong to components and 3 to compounds: $K_2F_2-2K_2SO_4$; $K_2SO_4-2PbSO_4$; and a Compound X whose composition was not fully elucidated.

The field of potassium sulfate occupies the largest area (38.73%) and displaces the field of $K_2F_2 \cdot 2K_2SO_4$ in the direction of potassium fluoride, due to which this compound melts inside the system with decomposition. The compound $K_2SO_4 \cdot 2PbSO_4$ (melting without decomposition) retains its stability inside the reciprocal system and occupies a small portion of the surface (7.65%). The field of the compound of unclarified composition comes close to the just mentioned field. Two possibilities arise in connection with Compound X: 1) it is the compound $K_2SO_4 \cdot PbSO_4$ which was detected in the solidus of the system $K_2SO_4-PbSO_4$; 2) it is a triple heterosalt; for the determination of its composition the visual polythermal method alone is inadequate.

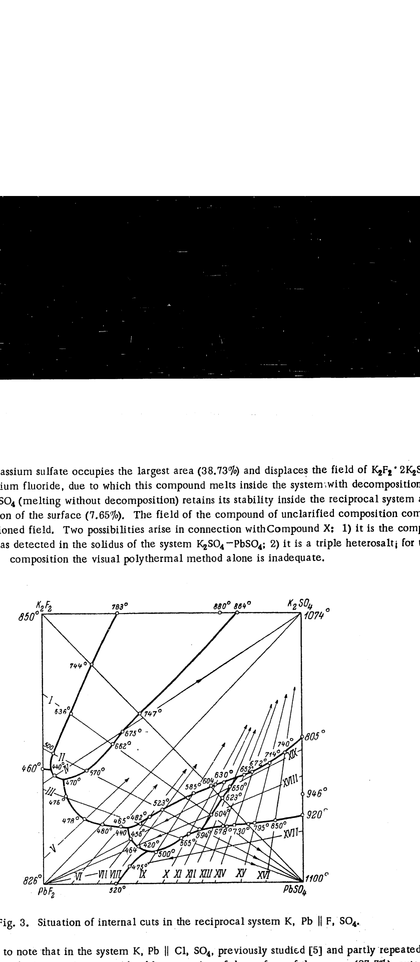

Fig. 3. Situation of internal cuts in the reciprocal system K, Pb || F, SO_4.

It is interesting to note that in the system K, Pb || Cl, SO_4, previously studied [5] and partly repeated by us, the field of $K_2SO_4 \cdot 2PbSO_4$ occupies a considerable proportion of the surface of the square (27.7%), extending nearly up to opposite side of the square. No other field was detected in this system. The absence of the field of X from the chloride system may be due either to its attack by chlorides or to the fact that it is a triple hetero compound which is only formed with fluorides but not with chlorides. In connection with our two suggestions about the character of the internal field, attention is now drawn to two variants of the triangulation of the reciprocal system.

First variant (Fig. 7), on the assumption that the field belongs to the double 1 : 1 compound ($K_2SO_4 \cdot PbSO_4$), the square of the reciprocal system is divided by three secants into 4 phase triangles:

I) $PbF_2-K_2F_2-K_2F_2 \cdot 2K_2SO_4$, II) $K_2F_2 \cdot 2K_2SO_4-PbF_2-K_2SO_4$,
III) $K_2SO_4 \cdot PbSO_4-PbF_2-K_2SO_4$, IV) $PbSO_4-PbF_2-K_2SO_4 \cdot PbSO_4$.

To each triangle corresponds a triple invariant point: E_1 440°, P 470°, E_2 440°, E_3 420°.

Second variant (Fig. 8) on the assumption that field X belongs to a triple heterocompound, the square of the reciprocal system is divided into 6 phase triangles:

I) $PbF_2-K_2F_2-K_2F_2 \cdot 2K_2SO_4$, II) $K_2F_2 \cdot 2K_2SO_4-PbF_2-K_2SO_4$,
III) $K_2SO_4-PbF_2-X$, IV) $K_2SO_4-X-K_2SO_4 \cdot 2PbSO_4$,
V) $K_2SO_4 \cdot 2PbSO_4-X-PbSO_4$ VI) $X-PbF_2-PbSO_4$.

To each of these triangles corresponds a triple invariant point, the temperature and composition of which are set forth in Table 5.

The experimental data for the composition and melting point of the triple invariant points are made more precise by projection of the curves of common crystallization on to the side of $PbSO_4-K_2SO_4$ (Fig. 9).

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TABLE 2
Internal Cuts of the Reciprocal System

Cut I		Cut II		Cut III		Cut XVIII		Cut XIX	
30% PbF_2, 70% K_2F_2 } $PbSO_4$		50% PbF_2, 50% K_2F_2 } $PbSO_4$		65% PbF_2, 35% K_2F_2 } $PbSO_4$		40% K_2SO_4, 60% $PbSO_4$ } PbF_2		50% K_2SO_4, 50% $PbSO_4$ } PbF_2	
% $PbSO_4$	Temp.	% $PbSO_4$	Temp.	% $PbSO_4$	Temp.	% PbF_2	Temp.	% PbF_2	Temp.
5	700°	2	523°	2	508°	10	840°	10	822°
10	648	4	517	6	490	16	792	13	794
13	663	6	554	8	480	19	762	19	743
15	682	10	576	10	516	22	733	22	713
20	695	13	577	13	532	26	692	24	694
23	686	15	574	18	542	29	663	26	676
26	664	17	580	20	542	32	633	29	665
29	686	20	603	26	534	35	606	32	644
32	692	23	613	29	524	38	598	35	634
35	691	26	614	35	495	41	592	41	608
41	672	32	603	38	500	47	573	46	580
47	633	38	574	41	524	51	558	52	547
53	574	44	532	44	540	56	546	56	527
56	564	47	538	47	552	59	522	59	506
59	584	50	557	50	560	62	501	62	487
62	598	56	585	53	572	64	472	65	465
65	636	59	595	56	622	66	470	68	450
68	668	62	650	59	672	68	508	71	484
71	727	65	700	65	760	71	534	74	516
78	850	71	795	71	832	74	564	76	536
Intersection 636°, 10.5% $PbSO_4$; 662°, 26% $PbSO_4$; 558°, 55% $PbSO_4$; 604°, 64% $PbSO_4$; 678°, 70% $PbSO_4$.		Intersection 500°, 3.5% $PbSO_4$; 570°, 16.5% $PbSO_4$; 523°, 45% $PbSO_4$; 595°, 59% $PbSO_4$.		Intersection 476°, 8.5% $PbSO_4$; 482°, 37% $PbSO_4$; 565°, 52.5% $PbSO_4$.		Intersection 604°, 34% PbF_2; 452°, 65% PbF_2.		Intersection 650°, 28% PbF_2; 456°, 67.5% PbF_2.	

TABLE 3
Internal Cuts of the Reciprocal System

Cut IV		Cut IX		Cut X		Cut XI		Cut XII	
37.5% K_2F_2, 62.5% PbF_2 } K_2SO_4		35% $PbSO_4$, 65% PbF_2 } K_2SO_4		45% $PbSO_4$, 55% PbF_2 } K_2SO_4		50% $PbSO_4$, 50% PbF_2 } K_2SO_4		55% $PbSO_4$, 45% PbF_2 } K_2SO_4	
% K_2SO_4	Temp.	% K_2SO_4	Temp.	% K_2SO_4	Temp.	% K_2SO_4	Temp.	% K_2SO_4	Temp.
0	502°	0	623°	8	672°	6	731°	10	740°
2	482	6	590	12	640	10	700	14	710
3	464	10	540	16	603	14	666	18	677
6	511	12	521	18	578	18	623	22	640
10	554	14	520	20	580	20	602	23	627
13	593	16	528	23	583	23	603	26	626
20	633	19	540	26	592	26	612	29	633
26	663	23	548	32	605	29	618	32	638
29	674	26	568	35	608	32	624	35	643
32	700	32	582	38	632	35	628	38	648
35	721	34	594	41	672	38	644	41	661
38	736	35	604	44	705	41	682	44	707
41	752	41	682	47	737	44	722	47	743
47	786	47	752	53	793	50	780	50	774
Intersection 464°, 4% K_2SO_4; 675°, 30% K_2SO_4.		Intersection 500°, 11.5% K_2SO_4; 585°, 34% K_2SO_4.		Intersection 567°, 18.5% K_2SO_4; 610°, 36.5% K_2SO_4.		Intersection 594°, 20.5% K_2SO_4; 630°, 27% K_2SO_4.		Intersection 620°, 23.5% K_2SO_4; 552°, 40.5% K_2SO_4.	

Fig. 4. Internal cuts of the reciprocal system. I -IV and IX-XI.

Fig. 5. Internal cuts of the reciprocal system. V-VIII and XVII-XIX.

TABLE 4
Internal Cuts of the Reciprocal System

Cut VII		Cut VIII		Cut XIII		Cut XV		Cut XVI	
80% PbF_2, 20% $PbSO_4$ } K_2SO_4		75% PbF_2, 25% $PbSO_4$ } K_2SO_4		40% PbF_2, 60% $PbSO_4$ } K_2SO_4		25% PbF_2, 75% $PbSO_4$ } K_2SO_4		15% PbF_2, 85% $PbSO_4$ } K_2SO_4	
% K_2SO_4	Temp.	% K_2SO_4	Temp.	% K_2SO_4	Temp.	% K_2SO_4	Temp.	% K_2SO_4	Temp.
5	532°	5	532°	13	738°	14	862°	16	927°
8	508	8	508	18	700	18	826	20	890
11	484	11	485	20	682	20	811	23	850
14	460	14	472	23	688	23	788	26	858
20	492	17	495	26	698	26	807	29	860
23	498	20	507	32	688	29	808	32	858
26	511	23	514	35	670	32	800	38	840
29	538	26	522	38	657	38	770	44	798
32	570	29	532	41	678	41	747	47	770
35	592	32	555	48	765	44	720	50	762
		38	620	53	818	47	752	56	830
Intersection 456°, 15% K_2SO_4; 500°, 25% K_2SO_4.		Intersection 464°, 14% K_2SO_4; 532°, 29% K_2SO_4.		Intersection 678°, 20.5% K_2SO_4; 652°, 39% K_2SO_4.		Intersection 795°, 22% K_2SO_4; 714°, 44% K_2SO_4.		Intersection 850°, 23% K_2SO_4; 740°, 48.5% K_2SO_4.	

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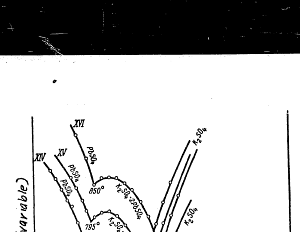

Fig. 6. Internal cuts of the reciprocal system. XII-XVI.

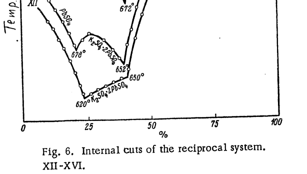

Fig. 7. Fusion diagram and triangulation of the reciprocal system K, Pb ‖ F, SO_4 (first variant). Explanation in text.

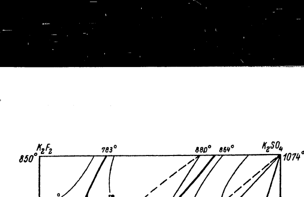

Fig. 8. Fusion diagram and triangulation of the reciprocal system K, Pb ‖ F, SO_4 (second variant). Explanation in text.

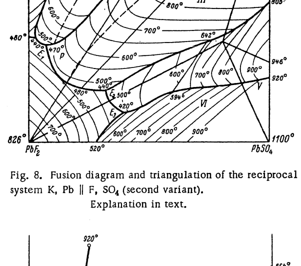

Fig. 9. Projection of the curves of common crystallization on the side of $PbSO_4-K_2SO_4$.

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TABLE 5

Point	Name	Temp.	Composition (in mol.-%)			
			PbF_2	$PbSO_4$	K_2F_2	K_2SO_4
E_1	Eutectic	440°	55.0	2.5	42.5	—
P_1	Transition	470	53.5	7.0	39.5	—
E_2	Eutectic	440	63.0	12.0	—	25.0
E_3	Eutectic	420	62.0	26.0	—	12.0
P_2	Transition	642	25.0	35.0	—	40.0
P_3	Transition	594	40.0	40.0	—	20.0

On comparing the chloride-sulfate reciprocal system [5] with the corresponding fluoride-sulfate system (K, Pb ‖ Cl, SO_4 and K, Pb ‖ F, SO_4), we observe that replacement of the chloride ion by the fluoride ion leads to marked development of a number of complex compounds both on the sides and inside the fluoride-sulfate reciprocal system.

Apart from the compound $K_2SO_4 \cdot 2PbSO_4$ which is common to both systems, the fluoride system contains the field of the compound $K_2F_2 \cdot 2K_2SO_4$ as well as an internal field of not fully elucidated composition. The thermochemical effects of the exchange reactions in these systems are: for the chloride-sulfate system 0.17 kcal/equiv. in the direction of $K_2Cl_2-PbSO_4$, and for the fluoride-sulfate system 6.84 kcal/equiv. in the direction of $PbF_2-K_2SO_4$.

The chloride-sulfate reciprocal system is an example of the adiagonal type of system, while the fluoride-sulfate system belongs to the diagonal type.

SUMMARY

1. The liquidus surface of the irreversible-reciprocal system K, Pb ‖ F, SO_4, consists of 7 fields of crystallization, of the components and 3 compounds: $K_2F_2 \cdot 2K_2SO_4$, $K_2SO_4 \cdot 2PbSO_4$ and a Compound X.

2. Inside the system the field of the compound $K_2F_2 \cdot 2K_2SO_4$ (melting without decomposition) is displaced by the field of potassium sulfate and passes over into the field of a compound melting with decomposition.

3. The compound $K_2SO_4 \cdot 2PbSO_4$ remains stable inside the system, as reflected in the rectangular form of its field of crystallization.

4. There are two possible interpretations of the internal field of the compound: a) it is a double compound with the composition $K_2SO_4 \cdot PbSO_4$ which was detected in the solidus of the binary system $K_2SO_4-PbSO_4$; or b) it corresponds to a triple heterocompound (melting with decomposition) of unclarified composition. A similar internal field was not detected in the corresponding chloride-sulfate reciprocal system. The most stable section is the diagonal cut of $PbF_2-K_2SO_4$; the adiagonal sections $K_2F_2 \cdot 2K_2SO_4-PbF_2$ and $K_2SO_4 \cdot 2PbSO_4-PbF_2$ bear a subordinate character.

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STUDY OF THE SYSTEMS SODIUM SULFATE – COBALT SULFATE AND SODIUM SULFATE – NICKEL SULFATE

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The system sodium sulfate – cobalt sulfate has been investigated by Calcagni and Marotta [1] by the method of cooling curves. According to their data the system belongs to the eutectic type. The eutectic crystallizes at a content of 50% cobalt sulfate and a temperature of 675°. On the sodium sulfate side is a region of solid solutions extending up to 33% cobalt sulfate. In melts containing from 18 to 45% cobalt sulfate, thermal effects were observed at 425° that corresponded to the double salt $CoSO_4 \cdot 3Na_2SO_4$ of the vanthoffite type.

The system sodium sulfate – nickel sulfate has not previously been studied.

The systems were investigated by the method of thermal analysis. Most of the data were obtained by recording the differential heating curves. The liquidus of the systems was established by recording of the cooling curves and also by the visual-polythermal method. The data of thermal analysis were confirmed by study of the microstructure of the melts and by study of the crystal optics. Melts were crystallized between two mica plates for preparation of specimens for study of microstructure.

Our plot of the phase diagram of the system sodium sulfate – cobalt sulfate (Fig. 1) contains three branches of crystallization. Line AB corresponds to crystallization from the melt of a solid solution on the basis of sodium sulfate. Branch BC corresponds to crystallization of a compound, which we designate ϵ, formed by a peritectic reaction (line CE) at a temperature of 590°. Judging by the point of termination of the eutectic line FG, and by analogy with the system sodium sulfate – magnesium sulfate [2], the formula $3CoSO_4 \cdot Na_2SO_4$ may be assigned to this compound. Cobalt sulfate crystallizes from melt along the line CD. The eutectic crystallizes at 565°. Its composition corresponds to a content of 49% cobalt sulfate. The region of solid solution on the basis of sodium sulfate extends at the eutectic temperature to a content of 38% cobalt sulfate.

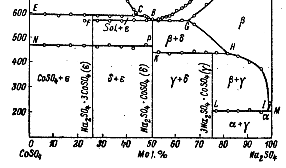

Fig. 1. Phase diagram of the system cobalt sulfate–sodium sulfate.

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Lowering of the temperature leads to decomposition of the solid solution along the lines GH and HI with formation of the compounds $CoSO_4 \cdot Na_2SO_4$ (δ) and $CoSO_4 \cdot 3Na_2SO_4$ (γ). The temperature of formation of Compound γ along the horizontal line KH is 440°.

We were unable to establish the temperature of formation of Compound δ. There are two possible explanations of this: This temperature is close to the eutectic temperature so that the effects of crystallization of the eutectic and of the formation of the compound substantially coincide (as shown in Fig. 1);alternatively, δ crystallizes directly from the melt and has an insignificant liquidus line which escaped our observation.

The horizontal line LM (205°) corresponds to a eutectoid transformation associated with the polymorphic transformation of sodium sulfate. The horizontal line NP (460°) must evidently be associated with the polymorphic transformation of Compound ϵ.

The system sodium sulfate – nickel sulfate (Fig. 2) is similar to that described above. The region of solid solutions extends to a content of 35% nickel sulfate. In this system, Compound δ has a well-marked maximum on the fusion diagram. Eutectic points correspond to contents of 41 and 55% nickel sulfate and temperatures of 671 and 700° respectively.

The Compound γ is formed in the solid state on the horizontal line IK at a temperature of 432°. Compound ϵ is evidently formed in the high-temperature unstable region. The presence of eutectic halts to the left of the ordinate of the compound is explained by the incompleteness of the reaction of formation of Compound ϵ under the experimental conditions; due to the thermal instability of nickel sulfate it is impossible either to bring the meltsto fusion point or to subjectthem to prolonged heating at above 700°.

Fig. 2. Phase diagram of the system nickel sulfate – sodium sulfate.

TABLE
Characteristics of the Double Compounds

Formula of compound	Color	Double refraction of light	Refractive index
$3Na_2SO_4 \cdot CoSO_4$	Light-violet	Weak	1.51
$Na_2SO_4 \cdot CoSO_4$	Pleochroism from violet to red-violet	Strong	1.53
$Na_2SO_4 \cdot 3CoSO_4$	Brownish-violet	Medium	1.70
$3Na_2SO_4 \cdot NiSO_4$	Light-yellow	Weak	1.50
$Na_2SO_4 \cdot NiSO_4$	Dark-yellow	Strong	1.54
$Na_2SO_4 \cdot 3NiSO_4$	Brown	Medium	1.74

In the table are set forth the characteristics of the compounds detected by us in the two binary systems on the basis of crystal-optical investigations.

Thus, compounds of the following types were found in both systems: $3Na_2SO_4 \cdot MeSO_4$, $Na_2SO_4 \cdot MeSO_4$ and $Na_2SO_4 \cdot 3MeSO_4$, where Me = Ni, Co.

SUMMARY

1. The phase diagrams of the binary systems of sodium sulfate with cobalt sulfate and nickel sulfate were studied.

2. Both systems are characterized by reciprocal solubility of the components in the liquid state, the formation of a broad region of solid solutions from the side of sodium sulfate, and the presence of three double compounds ($3Na_2SO_4 \cdot MeSO_4$, $Na_2SO_4 \cdot MeSO_4$ and $Na_2SO_4 \cdot 3MeSO_4$).

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CATION EXCHANGE IN MIXED SOLVENTS ON VOLKONSKOITE

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The question of the influence of the liquid phase upon the extent and character of exchange adsorption has acquired great importance at the present time in view of the extensive applications of ion exchange. A number of authors [1-8] have studied exchange adsorption in nonaqueous and mixed media and have observed a considerable influence of the liquid phase on the extent and the character of the exchange. In previous investigations we studied [6, 7] the dependence of the extent of adsorption on the dielectric constant of the liquid phase. In addition, the applicability of the equations of B. P. Nikolsky [9] and E. N. Gapon [10], which characterize the exchange from aqueous solutions, to exchange adsorption of cations from mixed solvents was checked.

The marked identity of the quantitative laws of exchange of cations from aqueous and mixed media and the influence of the dielectric constant of the solvent upon the magnitude of the adsorption present great practical, as well as theoretical, interest. For this reason we undertook the following investigations with the aim of gaining a deeper insight into the processes of ion-exchange adsorption from mixed solvents.

EXPERIMENTAL

In this research we studied the dependence of the magnitude of exchange of Ba-volkonskoite for $Na^{\cdot}$ and $K^{\cdot}$ ions from aqueous alcoholic and dioxane-water solutions of various concentrations.

The investigations were carried out on volkonskoite [11-13] from the Efimyatsky deposit; its adsorption capacity was approximately 100 mg-equiv. per 100 g adsorbent. In preliminary experiments it was established that volkonskoite is inert to the solvents investigated; it absorbs neither water nor alcohol nor dioxane.

TABLE 1
Ba-volkonskoite + NaCl

Alcohol (wt. %)	Concentration NaCl (in g-equiv/l)						
	0.025	0.050	0.075	0.100	0.150	0.200	0.250
	mg-equiv $Ba^{\cdot\cdot}$ *						
0	0.82	1.34	1.76	2.13	2.77	3.32	3.80
10	0.84	1.38	1.82	2.22	2.90	3.41	3.89
30	0.90	1.47	1.92	2.33	3.10	3.70	4.15
50	0.96	1.58	2.08	2.52	3.29	3.95	4.43
70	0.99	1.65	2.20	2.60	3.43	—	—

* displaced from 10 g Ba-volkonskoite

TABLE 2
Ba-volkonskoite + KCl

Alcohol (wt. %)	Concentration KCl (in g-equiv/l)						
	0.025	0.050	0.075	0.100	0.150	0.200	0.250
	mg-equiv $Ba^{\cdot\cdot}$ *						
0	1.94	3.46	4.66	5.59	6.80	7.60	8.02
10	2.04	3.72	5.02	6.00	7.29	7.95	8.28
30	2.15	4.12	5.58	6.60	7.78	8.32	8.56
50	2.18	4 24	5.75	6.87	7.93	8.47	8.64

* displaced from 10 g Ba-volkonskoite

The influence of the composition of the medium on the extent and character of exchange was studied on solutions of NaCl and KCl of various concentrations in various aqueous alcohol and aqueous dioxane solvents. The following procedure was adopted: 5 g lots of Ba-volkonskoite were placed in special small flasks with ground glass stoppers. Into each flask was then run 50 ml of a solution of specific composition concentration of salt, and the flasks then allowed to stand for 48 hours with frequent shaking. The flasks containing the settled equilibrium solutions were transferred to a thermostat, and at 25° samples were pipeted off and analyzed for the number of milligram-equivalents of desorbed $Ba^{\cdot\cdot}$.

The experimental data are presented in Tables 1 to 5.

TABLE 3
Ba-volkonskoite + NaCl + 50% Dioxane

NaCl concentration (in g-equiv/. l)	mg-equiv Ba·· displaced from 10 g Ba-volkonskoite
0.025	0.85
0.050	1.34
0.075	1.75
0.100	2.16
0.150	2.72

TABLE 4
Ba-volkonskoite + 0.1 N NaCl Solution

Dioxane (wt.-%)	mg-equiv Ba·· displaced from 10 g Ba-volkonskoite
0	2.13
10	2.16
30	2.09
50	2.16
70	2.26

TABLE 5
Ba-volkonskoite + 0.1 N KCl Solution

Dioxane (wt.-%)	mg-equiv Ba·· displaced from 10 g Ba-volkonskoite
0	5.59
20	5.74
30	5.95
40	6.12
50	6.22
70	6.26

The data show that desorption of Ba·· increases with falling dielectric constant of the medium. The influence of change of dielectric constant on the extent of exchange from aqueous dioxane solutions is less pronounced than from aqueous alcohol solutions, and in the case of exchange of [Ba··] + Na· the effect is completely reversed; the results obtained in the study of the exchange adsorption of [Ba··] + Na· from dioxane-water mixture containing 50 wt.-% dioxane are identical with those obtained in aqueous solution.

The influence of change of dielectric constant upon the extent of exchange is more marked in the region of high dielectric constants, the effect being insignificant in the region of low dielectric constants. Thus in the exchange of [Ba··] + K· in aqueous dioxane, identical results are obtained with dioxane contents of 50 and 70 weight-%.

On the basis of the experimental data we calculated the Gapon equation [10] of the exchange adsorption isotherm and our rearranged form of Nikolsky's equation [9, 6].

In its general form the Gapon equation may be written:

$$\frac{a_1}{a_2} = K\frac{C_1^{1/n_1}}{C_2^{1/n_2}}, \tag{1}$$

where a_1 and a_2 are the concentrations of the adsorbed cations in milligram-equivalents; C_1, C_2 are the equilibrium concentrations of the exbhanging cations in the solution in millimoles per 1 ml; n_1, n_2 are the valences of the exchanging cations; and K is the exchange constant.

For the case under investigation of exchange between divalent and monovalent ions, it has the form:

$$\frac{1}{a} = \frac{1}{a_m} + \frac{K}{a_m}\frac{\sqrt{\frac{a}{2}}}{100C_0 - a}, \tag{2}$$

where a is the amount of divalent cation in milligram-equivalents desorbed from 10 g adsorbent, equal to the number of milligram-equivalents of adsorbed monovalent cation, a_m is the maximum adsorption in milligram-equivalents per 10 g adsorbent, C_0 is the initial concentration of monovalent cation in millimoles per milliliter, and K is the exchange constant.

The above is a linear equation. Putting $y = \frac{1}{a}$; $x = \frac{\sqrt{\frac{a}{2}}}{100C_0 - a}$, we find the free term of the equation (a line intersecting the ordinate) equal to the reciprocal of the maximum adsorption. From the angular coefficient of the straight line K/a_m we find the value of K (the exchange constant).

Nikolsky proposed the following equation for characterization of the equilibrium state in exchange of ions of different valences:

$$\frac{a_1^{1/n_1}}{a_2^{1/n_2}} = K\frac{C_1^{1/n_1}}{C_2^{1/n_2}}, \tag{3}$$

where a_1, a_2 are the number of adsorbed cations in millimoles per 1 ml; n_1, n_2 are the valences of the exchanging ions; K is the exchange constant; C_1, C_2 are the equilibrium concentrations of cations in solution in millimoles per ml.

Starting from the procedure of the present investigation, Nikolsky's equation [9] was rearranged to give the linear equation [6]:

$$a = a_m - K^2 a\left(\frac{a}{100C_0 - a}\right)^2, \tag{4}$$

where a is the number of milligram-equivalents of the divalent cation desorbed from 10 g adsorbent, equal to the amount of adsorbed monovalent cation, a_m is the maximum adsorption in milligram-equivalents per 10 g adsorbent, C_0 is the initial concentration of monovalent cation in millimoles per 1 ml, and K is the exchange constant.

Putting $y = a$; $x = a\left(\frac{a}{100\ C_0 - a}\right)^2$ we find a_m as the length intercepted by the straight line at the ordinate, and K^2, the angular coefficient of the straight line.

The calculated values are set forth in Tables 6-9. The values of y, a_m and K were obtained by the method of least squares.

The data demonstrate the satisfactory applicability of Gapon's equation and of our rearranged form of Nikolsky's equation to exchange adsorption in mixed media. The applicability is confirmed by comparison with

σy, the mean square deviations of the individual determinations of y, $\left(\sigma_y = \sqrt{\frac{\Delta_i^2 g_i}{n}}\right)$,

and by comparison of the mean square errors of the mean values of the constants of the equations $\left(\sqrt{\frac{\Delta_i^2 g_i}{n(n-1)}}\right)$.

The applicability of the equations of exchange adsorption to the investigated systems confirms the previously noted identity of the quantitative laws in different solvents.

Analysis of Equations (2) and (4) shows that in the rearranged Nikolsky equation $x = \frac{a^3}{(100C_0 - a)^2}$ or $\ln x = 3 \ln a - 2 \ln (100C_0 - a)$; the relative error $\underline{x}$ is

$$\frac{dx}{x} = 3\frac{da}{a} + 2\frac{da}{100C_0 - a} = \frac{da}{a}\left(3 + \frac{2}{\frac{100C_0}{a} - 1}\right).$$

TABLE 6
Ba-volkonskoite + NaCl

Concentration of NaCl (in g-equiv./l)	Content of alcohol in aqueous alcohol solution (in weight-%) 0: x	0: $y_{calcd.}$	10: x	10: $y_{calcd.}$	30: x	30: $y_{calcd.}$	50: x	50: $y_{calcd.}$	70: x	70: $y_{calcd.}$
0.025	0.3811	1.222	0.3904	1.189	0.4192	1.117	0.4499	1.044	0.4660	1.006
0.050	0.2236	0.746	0.2295	0.725	0.2429	0.677	0.2599	0.632	0.2711	0.611
0.075	0.1634	0.564	0.1679	0.547	0.1756	0.509	0.1882	0.476	0.1979	0.463
0.100	0.1311	0.466	0.1354	0.454	0.1407	0.422	0.1501	0.394	0.1541	0.374
0.150	0.0962	0.361	0.0995	0.350	0.1046	0.331	0.1095	0.306	0.1132	0.291
0.200	0.0772	0.303	0.0787	0.290	0.0834	0.278	0.0876	[illegible]	—	—
0.250	0.0650	0.266	0.0661	0.254	0.0691	0.241	0.0724	[illegible]	—	—
	$a_m=14.3\pm0.4$ $K=43.2\pm1.5$ $\sigma_y=0.003$		$a_m=15.8\pm0.7$ $K=45.7\pm4.1$ $\sigma_y=0.003$		$a_m=14.3\pm1.0$ $K=35.8\pm3.0$ $\sigma_y=0.008$		$a_m=14.6\pm0.7$ $K=31.7\pm2.8$ $\sigma_y=0.003$		$a_m=16.1\pm2.6$ $K=32.5\pm6.1$ $\sigma_y=0.007$	

Note. Calculated from equation (2).

TABLE 7
Ba-volkonskoite + KCl

Concentration of KCl (in g-equiv./l)	Content of alcohol in aqueous alcohol solution (in weight-%) 0: x	0: $y_{calcd.}$	10: x	10: $y_{calcd.}$	30: x	30: $y_{calcd.}$	50: x	50: $y_{calcd.}$	70: x	70: $y_{calcd.}$
0.025	1.7588	0.512	2.1953	0.483	2.9623	0.440	3.2625	0.427	3.7629	0.442
0.050	0.8541	0.296	1.0655	0.282	1.6310	0.282	1.9158	0.287	1.7630	0.251
0.075	0.5375	0.220	0.6388	0.206	0.8700	0.192	0.9689	0.188	1.0294	0.181
0.100	0.3791	0.183	0.4330	0.169	0.5343	0.152	0.5921	0.149	0.6338	0.143
0.150	0.2249	0.146	0.2476	0.136	0.2732	0.121	0.2817	0.117	0.2857	0.109
0.200	0.1572	0.130	0.1655	0.121	0.1746	0.110	0.1785	0.106	—	—
0.250	0.1179	0.120	0.1217	0.114	0.1258	0.104	0.1270	0.101	—	—
	$a_m=10.93\pm0.2$ $K=2.61\pm0.09$ $\sigma_y=0.005$		$a_m=10.89\pm0.35$ $K=1.94\pm0.09$ $\sigma_y=0.007$		$a_m=11.19\pm2.2$ $K=1.33\pm0.3$ $\sigma_y=0.027$		$a_m=11.39\pm1.3$ $K=1.18\pm0.13$ $\sigma_y=0.025$		$a_m=12.16\pm1.0$ $K=1.16\pm0.16$ $\sigma_y=0.011$	

Note. Calculated from equation (2).

TABLE 8
Ba-volkonskoite + KCl

Concentration of NaCl (in g-equiv/l)	Content of alcohol in aqueous alcohol solution (in weight-%) 0: x	0: $y_{calcd.}$	10: x	10: $y_{calcd.}$	30: x	30: $y_{calcd.}$	50: x	50: $y_{calcd.}$	70: x	70: $y_{calcd.}$
0.025	0.1954	0.68	0.2151	0.87	0.2848	0.66	0.3731	0.81	0.4255	1.16
0.050	0.1796	1.32	0.2005	1.41	0.2549	1.53	0.3372	1.59	0.4002	1.59
0.075	0.1654	1.90	0.1868	1.92	0.2273	2.32	0.3064	2.26	0.3791	1.95
0.100	0.1560	2.28	0.1808	2.14	0.2150	2.68	0.2860	2.71	0.3210	2.94
0.150	0.1421	2.85	0.1666	2.66	0.2104	2.81	0.2598	3.28	0.3015	3.27
0.200	0.1315	3.28	0.1441	3.50	0.1906	3.39	0.2392	3.73	—	—
0.250	0.1220	3.66	0.1321	3.94	0.1643	4.15	0.2055	4.46	—	—
	$a_m=8.62\pm0.25$ $K=6.38\pm0.12$ $\sigma_y=0.11$		$a_m=8.82\pm0.37$ $K=6.08\pm0.16$ $\sigma_y=0.11$		$a_m=8.90\pm0.66$ $K=5.38\pm0.26$ $\sigma_y=0.27$		$a_m=8.93\pm0.3$ $K=4.66\pm0.12$ $\sigma_y=0.14$		$a_m=8.40\pm1.16$ $K=4.13\pm0.36$ $\sigma_y=0.22$	

Note. Calculated from eq. (4).

TABLE 9
Ba-volkonskoite + KCl

Concentration of KCl (in g-equiv/l)	Content of alcohol in aqueous alcohol solution (in wt. %) 0: x	0: $y_{calcd.}$	10: x	10: $y_{calcd.}$	70: x	70: $y_{calcd.}$
0.025	23.283	1.81	40.122	2.07	139.562	2.58
0.050	17.466	3.42	31.419	3.45	108.636	3.94
0.075	12.546	4.79	20.569	5.16	72.278	5.54
0.100	8.982	5.78	13.500	6.28	39.810	6.97
0.150	4.677	6.98	6.517	7.38	10.450	8.27
0.200	2.855	7.49	3.461	7.86	—	—
0.250	1.789	7.78	2.030	8.09	—	—
	$a_m=8.28\pm0.08$ $K=0.53\pm0.01$ $\sigma_y=0.16$		$a_m=8.41\pm0.11$ $K=0.40\pm0.01$ $\sigma_y=0.18$		$a_m=8.73\pm0.28$ $K=0.21\pm0.01$ $\sigma_y=0.27$	

Note. Calculated from eq. (4).

In Gapon's equation

$$x=\frac{\sqrt{\frac{a}{2}}}{100C_0-a}, \quad \ln x=\frac{1}{2}\ln\frac{a}{2}-\ln(100C_0-a);$$

the relative error $\underline{x}$:

$$\frac{dx}{x}=\frac{1}{2}\frac{da}{a}+\frac{da}{100C_0-a}=\frac{da}{a}\left(\frac{1}{2}+\frac{1}{\frac{100C_0}{a}-1}\right).$$

At low concentrations the ratio $\frac{100C_0}{a}\approx 2$, with rising concentration it increases; consequently, the limiting relative error $\underline{x}$ is increased in Equation (2) by a factor of approximately 1.5, and in Equation (4) by a factor of 5 in relation to the experimental error.

In the exchange of Ba-volkonskoite + KCl the ratio 100 C_0/a at low concentrations is close to unity, so that the calculated errors $\underline{x}$ for this system are greatly increased. However, it is difficult to attribute the inapplicability of Equation (4) to the system Ba-volkonskoite + KCl in a solvent containing 30 and 50 weight-% alcohol to the increase of the experimental error during the calculation.

A comparison of the calculated data shows that neither the dielectric constant of the solvent nor its chemical character influences the value of the maximum adsorption. The difference in its values, calculated during investigation of the exchange in different media, fluctuated within the limits of experimental errors.

The fall in the K of exchange with increasing content of alcohol in aqueous alcohol mixtures testifies to the increased exchange with falling dielectric constant of the medium in the systems investigated.

SUMMARY

1. The exchange of Ba·· with Na· and K· ions from aqueous, aqueous alcohol and aqueous dioxane solvents on volkonskoite was studied.

2. The investigated quantitative laws of exchange of ions in mixed media are fully identical with the previously established laws of exchange in aqueous solutions.

3. Satisfactory constancy of the maximum adsorption is maintained in different solvents with differing dielectric constants.

4. The extent of exchange adsorption in the investigated systems increases with rising dielectric constant of the medium.

5. The difference in the values obtained for the exchange constants during adsorption of K· and Na· suggests the possibility of utilizing volkonskoite for the separation of those cations. It must be remembered, however, that the formation of potassium- or sodium-volkonskoite creates layers which are difficulty permeable by solutions.

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THIOCYANATE-HALIDE COMPLEXES OF DIVALENT MERCURY IN SOLUTION

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Halide complexes of divalent mercury have been the subject of fairly detailed study, whereas the thiocyanate complexes, in particular $HgCNS^+$ and $Hg(CNS)_2$ have been rather neglected. As far as we know, no attention has been given to the possibility of existence of mixed thiocyanate-halide complexes of mercury or to their stability.

For the purpose of determining the stability of the complex $Hg(CNS)_2$ in solution and for establishment of the conditions of formation and evaluation of the stability of some mixed thiocyanate-halide complexes of mercury, we made a study by the optical method of the equilibria in the systems:

$$Hg(NO_3)_2-KCNS-Fe(NO_3)_3-KCl \text{ and } Hg(NO_3)_2-KCNS-Fe(NO_3)_3-KBr.$$

EXPERIMENTAL

The following starting solutions were used: 0.05 M solution of $Hg(NO_3)_2$, 0.1 M solution of KCNS, 0.3 M solution of $Fe(NO_3)_3$ and 0.1 M solutions of KCl and KBr. All solutions were prepared from chemically pure or pure-for-analysis grades. The concentration of the solutions was determined by the usual methods of gravimetric and volumetric analysis. Mixtures each with a total volume of 50 ml were made up for investigation.

Eight series of experiments were carried out to study the above-mentioned equilibria. In each series mixtures were originally prepared that contained only ferric nitrate and potassium thiocyanate; only $FeCNS^{2+}$ was then formed in the system according to the equation:

$$Fe^{3+} + CNS^- = FeCNS^{2+}. \qquad \text{(a)}$$

Due to the presence of excess ferric nitrate in the system, the possibility of formation of other iron-thiocyanate complexes was substantially excluded. This was also confirmed by the constancy of the values of the molar coefficients of extinction (ϵ) for a given wavelength (λ) at various ratios of concentrations of Fe^{3+} and CNS^-. Hydrolysis in the investigated systems could not be at all significant, for the concentration of HNO_3 in the solution was 0.15 M. The ionic strength of the solution, due to HNO_3 and $Fe(NO_3)_3$, was 0.35.

The molar extinction coefficient of $FeCNS^{2+}$ was found from these experiments by measurement of the optical density of solutions on the FM photometer with an effective wavelength of 496 mμ or on the König-Martens spectrophotometer at λ 560 mμ and a cell length of 1 cm. All measurements were at 25 ± 1°.

After determination of the molar extinction coefficient, which was equal to 3500 ± 30 at λ_{eff} 496 mμ and 2000 ± 20 at 560 mμ, mercuric nitrate was introduced into System (a) in such amount that substantially the whole of the mercury was bound as mercuric thiocyanate:

$$Hg^{2+} + 2CNS^- = Hg(CNS)_2. \qquad \text{(b)}$$

During this reaction part of the $FeCNS^{2+}$ was decomposed due to displacement of the equilibrium of (a) to the left. The minimum value of the optical density (D') corresponds to this in Figs. 1 and 2. Formation of detectable amounts of $Hg(CNS)_3^-$ was excluded since the equilibrium concentration of CNS^- in solution was very small due to the presence of excess ferric nitrate.

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Examination was then made of mixtures of the four components – mercuric nitrate, potassium thiocyanate, ferric nitrate and potassium chloride (or bromide). The concentrations of the first three components remained constant in this experimental series, and only the original concentrations of chloride or bromide were varied.

In this case, apart from equilibria (a) and (b), we also have the equilibrium:

$$Hg(CNS)_2 + 2X^- = HgX_2 + 2CNS^-, \tag{c}$$

or even the equilibria:

$$Hg(CNS)_2 + X^- = Hg(CNS)X + CNS^-, \tag{I}$$

$$Hg(CNS)X + X^- = HgX_2 + CNS^-, \tag{II}$$

where $X^- = Cl^-$ or Br^-.

The thiocyanate displaced by the halide immediately gave fresh amounts of $FeCNS^{2+}$, and the optical density (D) increased, as seen from Figs. 1 and 2.

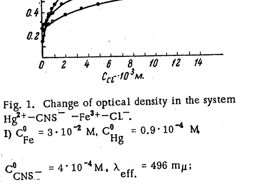

Fig. 1. Change of optical density in the system $Hg^{2+}-CNS^- -Fe^{3+}-Cl^-$.
I) $C^0_{Fe} = 3\cdot 10^{-2}$ M, $C^0_{Hg} = 0.9\cdot 10^{-4}$ M,

$C^0_{CNS^-} = 4\cdot 10^{-4}$ M., $\lambda_{eff.} = 496$ mμ;

II) $C^0_{Fe} = 3\cdot 10^{-2}$ M, $C^0_{Hg} = 1.8\cdot 10^{-4}$ M,

$C^0_{CNS^-} = 4\cdot 10^{-4}$ M, $\lambda_{eff.} = 496$ mμ;

III) $C^0_{Fe} = 3\cdot 10^{-2}$ M., $C^0_{Hg} = 4.5\cdot 10^{-5}$ M..

$C^0_{CNS^-} = 2\cdot 10^{-4}$ M, $\lambda_{eff.} = 496$ mμ;

IV) $C^0_{Fe} = 1.6\cdot 10^{-2}$ M, $C^0_{Hg} = 2.4\cdot 10^{-4}$ M,

$C^0_{CNS^-} = 6.6\cdot 10^{-4}$ M, $C^0_{KNO_3} = 1$ M, $\lambda = 560$ mμ.

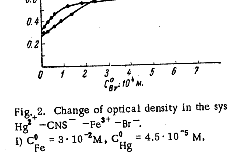

Fig. 2. Change of optical density in the system $Hg^{2+}-CNS^- -Fe^{3+}-Br^-$.
I) $C^0_{Fe} = 3\cdot 10^{-2}$M., $C^0_{Hg} = 4.5\cdot 10^{-5}$ M,

$C^0_{CNS^-} = 4\cdot 10^{-4}$ M, $\lambda_{eff.} = 496$ m μ;

II) $C^0_{Fe} = 3\cdot 10^{-2}$ M, $C^0_{Hg} = 9.0\cdot 10^{-5}$ M,

$C^0_{CNS^-} = 4\cdot 10^{-4}$ M, $\lambda_{eff.} = 496$ mμ;

III) $C^0_{Fe} = 3\cdot 10^{-2}$ M, $C^0_{Hg} = 4.5\cdot 10^{-5}$ M,

$C^0_{CNS^-} = 2\cdot 10^{-4}$ M, $\lambda_{eff} = 496$ mμ;

IV) $C^0_{Fe} = 1.6\cdot 10^{-2}$ M, $C^0_{Hg} = 2.4\cdot 10^{-4}$ M,

$C^0_{CNS^-}$ – $6.6\cdot 10^{-4}$ M, $\lambda = 560$ mμ.

In addition to the above-mentioned equilibria, still another equilibrium was developed in this complex system:

$$Fe^{3+} + X^- = FeX^{2+}. \tag{III}$$

In the relevant experiments it was shown that the colored complexes of $FeCl^{2+}$ and $FeBr^{2+}$ that were formed did not, within the range of our concentrations, distort the optical density which was the foundation of all our calculations.

The dependence of the magnitude of the optical density in mixtures of $Hg(NO_3)_2-KCNS-Fe(NO_3)_3-KCl(KBr)$ on the amount of added chloride or bromide is plotted in Figs. 1 and 2, and the results are also presented in Tables 1-4.

DISCUSSION OF RESULTS

If we assume that equilibrium (c) exists in the investigated mixtures after addition of the halide, then the equilibrium constant can be written:

$$K = \frac{[Hg(CNS)_2]\,[X^-]^2}{[HgX_2]\,[CNS^-]^2}.$$

The "constant" calculated on the basis of this assumption changes by a factor of several tens or hundreds in the investigated range of chloride or bromide concentrations. This is clear evidence that the reaction does not go according to Scheme (c) but stepwise according to Schemes (I) and (II).

Calculation of the stepwise equilibrium constants confirms this assumption, since the equilibrium constants in this case do indeed remain constant.

The equilibrium constant of Reaction (I):

$$K_I = \frac{[Hg(CNS)X]\,[CNS^-]}{[Hg(CNS)_2]\,[X^-]} \tag{1}$$

can be calculated if we know the initial concentrations of the starting reactants and one of the equilibrium concentrations. In the present case it is most convenient to calculate the equilibrium concentration of the thiocyanate since it is related in the simplest fashion to the equilibrium concentration of $FeCNS^{2+}$ which is directly determined by experiment:

$$C_{CNS^-} = K_{FeCNS^{2+}}\,\frac{C_{FeCNS^{2+}}}{C_{Fe^{3+}}} \tag{2}$$

As the calculation shows, the equilibrium concentration of iron ($C_{Fe^{3+}}$) in our experiments differs little from the initial concentration ($C^0_{Fe^{3+}}$). The value assumed for the instability constant of iron thiocyanate ($K_{FeCNS^{2+}}$) is $5\cdot 10^{-3}$ [1]. The concentration of the colored complex was found from the generally known expression:

$$C_{FeCNS^{2+}} = \frac{D}{\epsilon\, l}, \tag{3}$$

where D is the optical density, ϵ is the molar extinction coefficient, and l is the length of the cell (in cm).

By substitution in Equations (2) and (3) we find:

$$C_{CNS^-} = \frac{K_{FeCNS^{2+}}}{C^0_{Fe}\,\epsilon\, l} \tag{2a}$$

Since the expression

$$\frac{K_{FeCNS^{2+}}}{C^0_{Fe}\,\epsilon\, l} = \alpha \tag{2b}$$

will be constant for each series of experiments, Equation (2a) must finally assume the form:

$$C_{CNS^-} = \alpha D. \tag{4}$$

We find the equilibrium concentration of Hg(CNS) X from the difference in optical density before addition (D') and after addition (D) of the halide.

The concentration of the complex Hg(CNS)X will evidently be equal to that amount of thiocyanate which is formed as a result of displacement according to Scheme (I). Since part of the displaced thiocyanate is bound in the complex $FeCNS^{2+}$, it is clear that

$$C_{Hg(CNS)X} = (C_{FeCNS^{2+}} - C'_{FeCNS^{2+}}) + (C_{CNS^-} - C'_{CNS^-}), \tag{5}$$

TABLE 1
Equilibrium Constant of the Reaction $Hg(CNS)_2 + Cl^- = Hg(CNS)Cl + CNS^-$

Expt. No.	Optical density (D)	Initial concentration of chloride ($C^0_{Cl} \cdot 10^4 M$)	Constant $K^{Cl}_I \cdot 10^2$	Ratio of complex forms (in %)		
				$Hg(CNS)_2$	$HgCl_2$	$Hg(CNS)Cl$
Series I						
$C^0_{Fe} = 3 \cdot 10^{-2}$ M., $C^0_{Hg} = 9 \cdot 10^{-5}$ M., $C^0_{CNS} = 4 \cdot 10^{-4}$ M., $\lambda_{eff.} = 496$ mμ.						
1	0.640	0	—	100	—	—
2	0.690	2.8	3.3	80	1	19
3	0.730	5.6	3.8	65	2	33
4	0.785	11.2	4.6	42	4	54
5	0.830	19.6	5.5	28	7	65
Series II						
$C^0_{Fe} = 3 \cdot 10^{-2}$ M., $C^0_{Hg} = 1.8 \cdot 10^{-4}$ M., $C^0_{CNS} = 4 \cdot 10^{-4}$ M., $\lambda_{eff.} = 496$ mμ						
1	0.150	0	—	100	—	—
2	0.385	5.6	3.3	54.3	3.7	42
3	0.435	8.4	3.4	45.0	5.0	50
4	0.470	11.2	3.5	38.6	6.4	55
5	0.530	16.8	4.1	26.4	8.6	65
Series III						
$C^0_{Fe} = 3 \cdot 10^{-2}$ M., $C^0_{Hg} = 4.5 \cdot 10^{-5}$ M., $C^0_{CNS} = 2 \cdot 10^{-4}$ M., $\lambda_{eff.} = 496$ mμ						
1	0.268	0	—	100	—	—
2	0.295	1.1	4.2	92.7	0.3	7
3	0.320	2.2	4.5	85.9	0.6	13.5
4	0.360	4.4	5.1	75.0	1.0	24
5	0.400	8.8	4.8	62 0	2.0	36
Series IV						
$C^0_{Fe} = 1.6 \cdot 10^{-2}$ M., $C^0_{Hg} = 2.4 \cdot 10^{-4}$ M., $C^0_{CNS} = 6.6 \cdot 10^{-4}$ M., $C_{KNO_3} = 1$ M., $\lambda = 560$ mμ						
1	0.237	0	—	100	—	—
2	0.260	1.1	4.6	92.7	0.3	7
3	0.300	5.5	3.5	79.0	1.0	20
4	0.320	8.8	3.3	70.0	2.0	28
5	0.375	21.0	3.3	52.0	4.0	44
6	0.430	35.0	4.7	31.0	6.0	63

where $C'_{FeCNS^{2+}}$ and C'_{CNS^-} are the equilibrium concentrations of the colored complex and of the thiocyanate before addition of halide, while $C_{FeCNS^{2+}}$ and C_{CNS^-} are the concentrations after addition of halide. Slightly rearranging Equation (5) with the help of Equations (3) and (4), we find:

$$C_{Hg(CNS)X} = \frac{1}{\epsilon l}\,(D-D') + \alpha\,(D-D'). \tag{5a}$$

Finally, if we put

$$\frac{1}{\epsilon l} = \gamma, \tag{5b}$$

and denote by ΔD the difference of optical density after addition of halide (D) and before addition of halide (D'), we obtain:

$$C_{Hg(CNS)X} = (\gamma + \alpha)\,\Delta D. \tag{5c}$$

Since the equilibrium concentration of Hg^{2+} will be a vanishingly small magnitude ($< 10^{-10}$ M) in our experiments, then the equilibrium concentration of mercuric thiocyanate is expressed through the initial concentration of mercury and the equilibrium concentration of the mixed complex in the following manner:

TABLE 2
Equilibrium Constant of the Reaction $Hg(CNS)_2 + Br^- = Hg(CNS)Br + CNS^-$

Expt. No.	Optical density (D)	Initial concentration of bromide ($C^0_{Br} \cdot 10^5 M$)	Constant K^{Br}_I	Ratio of complex forms (in %)		
				$Hg(CNS)_2$	$Hg(CNS)Br$	$HgBr_2$
Series I						
$C^0_{Fe} = 3 \cdot 10^{-2}$ M., $C^0_{Hg} = 4.5 \cdot 10^{-5}$ M., $C^0_{CNS} = 4 \cdot 10^{-4}$ M., $\lambda_{eff.} = 496$ mμ						
1	0.910	0	—	100	—	—
2	0.950	1.9	3.5	67.5	28	4.5
3	0.975	3.0	6.0	48.5	45	6.5
4	1.00	4.5	7.1	30.0	59	11
5	1.03	6.0	19.6	8.0	77	15
Series II						
$C^0_{Fe} = 3 \cdot 10^{-2}$ M., $C^0_{Hg} = 9 \cdot 10^{-5}$ M., $C^0_{CNS} = 4 \cdot 10^{-4}$ M., $\lambda_{eff.} = 496$ mμ						
1	0.640	0	—	100	—	—
2	0.680	1 5	3.9	83.5	14.5	2
3	0.720	3.0	5.8	67 5	29.0	3.5
4	0.750	4.5	3.9	53.5	38.0	8.5
5	0.780	6.0	4.5	41.5	46.0	12.5
6	0.900	12.0	80.0	2.0	62.0	36.0
Series III						
$C^0_{Fe} = 3 \cdot 10^{-2}$ M., $C^0_{Hg} = 4.5 \cdot 10^{-5}$ M., $C^0_{CNS} = 2 \cdot 10^{-4}$ M., $\lambda_{eff.} = 496$ mμ						
1	0.320	0	—	100	—	—
2	0.360	1.5	4.2	68.5	28	3.5
3	0.395	3.0	5.4	39.0	55	6.0
4	0.430	4.5	11.0	14.0	71	15.0
Series IV						
$C^0_{Fe} = 1.6 \cdot 10^{-2}$ M., $C^0_{Hg} = 2.4 \cdot 10^{-4}$ M., $C^0_{CNS} = 6.6 \cdot 10^{-4}$ M., $\lambda_{eff.} = 560$ mμ						
1	0.270	0	—	100	—	—
2	0.350	6.0	2.9	74	21	5
3	0.460	15.0	6.5	41	46	13
4	0.580	24.0	12.0	14	69	17

$$C_{Hg(CNS)_2} = C^0_{Hg^{2+}} - C_{Hg(CNS)X}. \tag{6}$$

Substituting in Equation (6) the values of $C_{Hg(CNS)X}$ from (5c), we obtain:

$$C_{Hg(CNS)_2} = C^0_{Hg^{2+}} - (\gamma + \alpha)\,\Delta D. \tag{6a}$$

If we substract from the initial concentration of halide the concentrations of mixed complex and iron-halide complex, we obtain the equilibrium concentration of the halide:

$$C_{X^-} = C^0_{X^-} - C_{Hg(CNS)X} - C_{FeX^{2+}} \tag{7}$$

Taking (5c) into account, Equation (7) can be written:

$$C_{X^-} = C^0_{X^-} - (\alpha + \gamma)\,\Delta D - C_{FeX^{2+}}. \tag{7a}$$

The last term of Equation (7a) is easily calculated from the expression for the equilibrium constant of Reaction (III):

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$$C_{FeX^{2+}} = \frac{C^0_{Fe} \cdot C_{X^-}}{K_{FeX^{2+}}} . \qquad (8)$$

The values of the instability constants of the complexes of $FeCl^{2+}$ and $FeBr^{2+}$ entering into Equation (8) are taken from a paper by Rabinowitch and Stockmayer [2] and are equal respectively to 0.24 and 2.

Substituting the expressions obtained for the equilibrium concentrations in Equation (1), we obtain in the final form the calculated formula for the equilibrium constant of Reaction (I):

$$K_1 = \frac{(\gamma + \alpha)\ \Delta D \cdot \alpha D}{[C^0_{Hg} - (\gamma + \alpha)\ \Delta D]\ [C^0_X - (\gamma + \alpha)\ \Delta D - C_{FeX^{2+}}]} . \qquad (9)$$

The calculated values of K_1 are given in Tables 1 and 2.

Table 1 shows that the values of K_1 are constant. The mean value from the series of measurements is $K^{Cl}_{I} = (4.0 \pm 0.3) \cdot 10^{-2}$.

We see from the data of the table that the displacement of thiocyanate by chloride from $Hg(CNS)_2$ proceeds already at the first stage of Reaction (c) with considerable difficulty and with a large excess of chloride. Even more difficult is the displacement of the second ion of thiocyanate; hence Reaction (I) is very slightly complicated by Reaction (II) over a large interval of chloride concentrations. To demonstrate this, we calculated the ratio of the complex forms in percentages. The required concentrations of $Hg(CNS)_2$, $Hg(CNS)Cl$ or $Hg(CNS)Br$ were calculated as shown above. The initial concentration of mercury ($C^0_{Hg^{2+}}$) was known. The $HgCl_2$ concentration and the $HgBr_2$ concentration were found from the expression for the constant of Reaction (II) (see later).

In the case of displacement of thiocyanate from $Hg(CNS)_2$ by bromide, both of the processes (I) and (II) overlap to a large extent. We evaluated the values of K^{Br}_{I} for those concentrations of bromide at which not more than 10% $HgBr_2$ is formed and we obtained the mean value from a series of measurements: $K^{Br}_{I} = 4.7 \pm 0.7$.

When the calculation of the equilibrium according to Scheme (I) with utilization of Equation (6a) pointed to the absence of $Hg(CNS)_2$ from the mixture, we proceeded to calculate the equilibrium according to Scheme (II). The equilibrium constant of Reaction (II) may be written:

$$K_{II} = \frac{[HgX_2]\ [CNS^-]}{[Hg(CNS)X]\ [X^-]} . \qquad (10)$$

The equilibrium concentration of thiocyanate was determined from Equation (4). Equation (5c) is no longer suitable for calculation of the equilibrium concentration of mercury thiocyanate-chloride. We find it as the difference between the initial concentration of the thiocyanate ion and the equilibrium concentrations of the thiocyanate ion and ferric thiocyanate:

$$C_{Hg(CNS)X} = C^0_{CNS^-} - C_{CNS^-} - C_{FeCNS^{2+}} . \qquad (11)$$

Combining Equation (11) with (3), (4) and (5b), we obtain:

$$C_{Hg(CNS)X} = C^0_{CNS^-} - (\alpha + \gamma)\ D. \qquad (11a)$$

Since the concentration of $Hg(CNS)_2$ is vanishingly small, the equilibrium concentration of the mercury halide may be expressed as:

$$C_{HgX_2} = C^0_{Hg} - C_{Hg(CNS)X} - C_{HgX_3^-} . \qquad (12)$$

Here it is no longer possible to ignore the formation of HgX_3^-, since the concentrations of halide are very high:

$$HgX_2 + X^- = HgX_3^- . \qquad (IV)$$

The concentrations of HgX_3^- calculated from the expression for the equilibrium constant of Reaction (IV) are set forth in Tables 3 and 4.

TABLE 3*
Equilibrium Constant of the Reaction $Hg(CNS)Cl + Cl^- = HgCl_2 + CNS^-$

Expt. No.	Optical density (D)	Initial concentration of chloride ($C^0_{Cl} \cdot 10^4 M$)	Constant $K^{Cl}_{II} \cdot 10^3$	Ratio of complex forms (in %)		
				$Hg(CNS)Cl$	$HgCl_2$	$HgCl_3^-$
Series I						
1	0.995	112	1.3	78	20.5	1.5
2	1.035	282	1.1	62	32.5	5.5
Series II						
1	0.800	90	1.7	73	25.5	1.5
2	0.845	160	1.3	67	30.0	3.0
3	0.950	280	1.8	47	45.5	7.5
Series III						
1	0.680	141	1.1	87	12	1
2	0.750	352	1.3	69	25	6
3	0.770	704	0.8	62	26	12
4	0.760	1480	0.23	64	18	18
Series IV						
1	0.550	141	1.5	83	15.5	1.5
2	0.660	704	1.6	46	37	17

*For initial conditions see Table 1.

Combining Equation (12) and (11a) we obtain finally:

$$C_{HgX_2} = C^0_{Hg} - C^0_{CNS^-} + (\alpha + \gamma)\ D - C_{HgX_3^-} . \qquad (12a)$$

Finally, we find the equilibrium concentration of halide by substracting from its initial concentration the amounts going into the composition of the complex compounds:

$$C_{X^-} = C^0_{X^-} - 2C_{HgX_2} - C_{Hg(CNS)X} - C_{FeX^{2+}} - C_{HgX_3^-} . \qquad (13)$$

Inserting in Equation (13) the values of C_{HgX_2} and $C_{Hg(CNS)X}$ from Equations (12a) and (11a) and carrying out the elementary mathematical rearrangements, we obtain:

$$C_{X^-} = C^0_{X^-} - 2C^0_{Hg} + C^0_{CNS^-} - (\alpha + \gamma)\ D - C_{FeX^{2+}} + C_{HgX_3^-} . \qquad (13a)$$

Here we substitute the values derived for the equilibrium concentrations in Equation (10) and we obtain the following final expression for the equilibrium constant of Reaction (II):

(14)

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The values of constants calculated from Equation (14) are set forth in Tables 3 and 4.

With increasing concentration of chloride in the mixtures, the optical density only rises up to a certain limit and then starts to fall (an example is Experiment 4, Series III in Table 3). We assume that in this case the amount of $FeCNS^{2+}$ formed by displacement of thiocyanate according to Reaction (II) is smaller than that undergoing decomposition according to the reaction: $FeCNS^{2+} + Cl^- = FeCl^{2+} + CNS^-$.

Experiments on this step were abandoned since calculation according to Scheme (II) would have been extremely difficult.

From the data of Tables 3 and 4 we find the mean values of the constants $K_{II}^{Cl} = (1.4 \pm 0.2) \cdot 10^{-3}$ and $K_{II}^{Br} = 0.34 \pm 0.04$.

The values obtained for the equilibrium constants of Reactions (I) and (II) enable us to calculate the instability constants of the thiocyanate-halide complexes and of mercury thiocyanate. For this purpose, we multiply and divide the right-hand side of Equation (1) by $[CNS^-]$ and the right-hand side of Equation (10) by $[X^-]$. We then obtain a slightly different expression for the equilibrium constants of Reactions (I) and (II).

$$K_I = \frac{K_{Hg(CNS)_2}}{K_{Hg(CNS)X}}, \qquad (15)$$

$$K_{II} = \frac{K_{Hg(CNS)X}}{K_{HgX_2}}, \qquad (16)$$

where $K_{Hg(CNS)_2}$, $K_{Hg(CNS)X}$ and K_{HgX_2} are instability constants of the respective compounds.

TABLE 4 *

Equilibrium Constant of the Reaction $Hg(CNS)Br + Br^- = HgBr_2 + CNS^-$

Expt. No.	Optical density (D)	Initial concentration of bromide ($C^0_{Br} \cdot 10^5$ M)	Constant K_{II}^{Br}	Ratio of complex forms (in %)		
				$Hg(CNS)Br$	$HgBr_2$	$HgBr_3^-$
Series I						
1	1.13	24	0.26	53	45	2
2	1.14	36	0.29	38	57	5
3	1 15	40	0.34	31	63	6
4	1.17	48	0.45	22	71	7
Series II						
1	1.03	24	0.23	63	36	1
2	1.08	36	0.28	45	52	3
3	1.10	42	0.30	37	58	5
4	1.12	48	0.33	31	63	6
Series III						
1	0.530	12	0.37	55	44.4	0.6
2	0.550	18	0.39	38	60	2
Series IV						
1	0.740	45	0.34	71	28	1
2	0.810	60	0.47	52	45	3
3	0.850	75	0.43	43	52	5
4	0.900	120	0.41	27	61	12
5	0.917	150	0.39	22	61	17

Taking for the instability constant of mercuric chloride (K_{HgCl_2}) the value $6.0 \cdot 10^{-14}$, and for mercuric bromide (K_{HgBr_2}) the value $4.7 \cdot 10^{-18}$, as reported in the literature [3], we find from Equation (13) the instability constants of the thiocyanate-chloride complex $K_{Hg(CNS)Cl} = 8.4 \cdot 10^{-17}$ and of the thiocyanate-bromide complex $K_{Hg(CNS)Br} = 1.6 \cdot 10^{-18}$.

* For initial conditions see Table 2.

The above values of K_I^{Cl} and $K_{Hg(CNS)Cl}$, after substitution in Equation (15), enable us to find the magnitude of the instability constant of mercuric cyanide: $K_{Hg(CNS)_2} = 3.4 \cdot 10^{-18}$. The very same calculations with utilization of K_I^{Br} and $K_{Hg(CNS)Br}$ give for $K_{Hg(CNS)_2}$ a value of $7.5 \cdot 10^{-18}$. Of the two values of $K_{Hg(CNS)_2}$ obtained by different routes, we consider the value of $3.4 \cdot 10^{-18}$ to be the more trustworthy.

The results of the present investigation undoubtedly confirm the existence in aqueous solution of mixed thiocyanate-halide complexes capable of existing in presence of a large excess of halide and distinguished by great stability.

The literature data for mixed complexes of mercury are also consistent with the existence of mixed mercury thiocyanate-halides. Thus, for example, a study of the Raman spectra of mixtures of alcoholic solutions of $HgBr_2$ and $HgCl_2$, HgBr and $Hg(CN)_2$, $HgCl_2$ and $Hg(CN)_2$ by several authors [4, 5] revealed the presence of halide and cyanohalide complexes HgClBr, Hg(CN)Br and Hg(CN)Cl.

There are indications that Hg^{2+} forms stable mixed pyridinosalicylate complexes [6], etc.

Unfortunately, there are no data for the stability of mixed complexes of mercury (or for many other complex formers) in aqueous solutions; such data would have enabled us to analyze the character of their stability and formation.

It is interesting to note that in the compounds Hg(CNS)Br and Hg(CNS)Cl the chemical affinity of the addends in aqueous solution is greater than the sum of the individual mean values of chemical affinity of the addends in the simple complexes of $HgBr_2$ and $Hg(CNS)_2$ or $HgCl_2$ and $Hg(CNS)_2$. A similar feature of pyridinosalicylate complexes of copper was pointed out by A. K. Babko [7] in a study of the conditions of their formation.

The stability of $Hg(CNS)_2$ was found to be similar to that of $HgBr_2$. This is fully understandable in the light of the fact that the most important properties of the addends Br^- and CNS^-, such as charge, radius, heat of hydration and electron affinity of their constituent atoms or atomic groups, are identical [8]. The value of the instability constant of $Hg(CNS)_2$ that we found is very different from the value of $2 \cdot 10^{-20}$ given in the literature [9].

The results of the above investigations can be utilized for selection of optimum conditions of mercurimetric determination of CNS^- and also of mixture of Br^- and CNS^-.

SUMMARY

1. A study was made by the optical method of the equilibrium in the systems: $Hg(NO_3)_2 - KCNS - Fe(NO_3)_3 - KCL$ and $Hg(NO_3)_2 - KCNS - Fe(NO_3)_3 - KBr$. The stepwise character of the reaction $Hg(CNS)_2 + 2X^- = HgX_2 + 2CNS^-$ (where $X = Cl^-$ or Br^-) was demonstrated; in this reaction the formation in solution of mixed thiocyanate-halide complexes Hg(CNS)Br and Hg(CNS)Cl was established.

2. The equilibrium constants of the following reactions were found:

$$Hg(CNS)_2 + Cl^- = Hg(CNS)Cl + CNS^-, \; K_I^{Cl} = (4.0 \pm 0.3) \cdot 10^{-2};$$

$$Hg(CNS)Cl + Cl^- = HgCl_2 + CNS^-, \; K_{II}^{Cl} = (1.4 \pm 0.2) \cdot 10^{-3};$$

$$Hg(CNS)_2 + Br^- = Hg(CNS)Br + CNS^-, \; K_I^{Br} = 4.7 \pm 0.7;$$

$$Hg(CNS)Br + Br^- = HgBr_2 + CNS^-, \; K_{II}^{Br} = 0.34 \pm 0.04.$$

3. The values of the instability constants of the complexes Hg(CNS)Br, Hg(CNS)Cl and $Hg(CNS)_2$, were determined: $K_{Hg(CNS)Br} = 1.6 \cdot 10^{-18}$, $K_{Hg(CNS)Cl} = 8.4 \cdot 10^{-17}$, $K_{Hg(CNS)_2} = 3.4 \cdot 10^{-18}$.

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DETERMINATION OF THE SOLUBILITY OF $Co[Hg(CNS)_4]$

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Ammonium tetrathiocyanomercuroate has found wide application in qualitative and quantitative analysis [1-13]. It is employed for precipitation of salts of some divalent cations, such as $Co^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Zn^{\cdot\cdot}$ and others, in the form of $Me[Hg(CNS)_4]$. The study of the properties of compounds of this type, and in particular their solubility, is of undoubted practical and theoretical interest.

In the present research we studied the solubility of $Co[Hg(CNS)_4]$. In the literature on this subject we found only one paper, by B. V. Cuvelier [14], which described the determination of the solubility of cobalt tetrathiocyanomercuroate in water and in aqueous solutions of ammonium, potassium and sodium chlorides. His experimental technique was not distinguished by great accuracy and only permitted determination of solubility at relatively high temperatures (40-60°). We investigated the solubility of this salt by the radiometric micro method, using radioactive cobalt Co^{60}.

The studies of I. V. Tanaev [15-17] have shown how important is the study of the solubility of precipitated salts in aqueous solutions of electrolytes.

Our problem was the determination of the solubility of $Co[Hg(CNS)_4]$ both in water and in aqueous solutions of some electrolytes in various concentrations and at various temperatures. We used a solution of cobalt nitrate containing Co^{60} as radioactive indicator. The total concentration of cobalt in solution was 10.8 mg/ml; 0.25 ml of this solution was treated with 0.25 ml ammonium tetrathiocyanomercuroate*. A blue crystalline precipitate of $Co[Hg(CNS)_4]$ quickly came down when the reactants were in these ratios. The precipitate was stirred, allowed to stand, and after a few minutes it was centrifuged. The mother liquor was removed and the precipitate washed several times with water. The washed precipitate was transferred to a small beaker and 2 ml of the appropriate solvent was added. The beaker was placed in a jacketed vessel connected to a thermostat. The precipitate was stirred with a magnetic stirrer.

The experimental procedure consisted in preparation of a saturated solution of the investigated substance at the temperature of interest to us and determination of the radioactivity of a known volume of the saturated solution. This activity was compared with a standard possessing a known specific activity.

We established the instant of saturation of the solution of cobalt tetrathiocyanomercuroate by withdrawing samples at definite time intervals (1 hour) and measuring their activity. Samples continued to be taken off until constant activity was attained; this point corresponded to saturation of the solution. The solubility was calculated from the formula:

$$S = \frac{A_x \cdot 1000}{A_{sp.} \cdot 58.94}$$

where S is solubility of $C_0[Hg(CNS)_4]$ (mmol/l); A_x is the activity of the amount of cobalt present in 1 ml of saturated solution (impulses/min.); $A_{sp.}$ is the specific activity of 1 mg cobalt (impulses/min.); 58.94 is the atomic weight of cobalt.

The error in determination of the solubility did not exceed 2-3% of the measured magnitude.

* The reagent was prepared by dissolving 5 g $Hg(NO_3)_2$ and 5 g NH_4CNS in 6 ml distilled water.

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Results of determination of the solubility of cobalt tetrathiocyanomercuroate in water at various temperatures are set forth in Table 1. Saturation of the aqueous solutions of $Co[Hg(CNS)_4]$ was reached in 2 hours at the temperatures in question.

The temperature dependence shows that the solubility of the salt in water follows the general laws for the majority of precipitates of difficulty soluble compounds.

TABLE 1
Solubility of $Co[Hg(CNS)_4]$ in Water at Various Temperatures

Temperature	Solubility of $Co[Hg(CNS)_4]$ mmol/l
10°	1.09
20	1.46
30	1.98
40	2.68

TABLE 2
Solubility of $Co[Hg(CNS)_4]$ in Solutions of Electrolytes of Various Concentrations at 13.5°

Concentration of electrolyte (N)	Solubility of $Co[Hg(CNS)_4]$ (mmol/l)			
	NH_4CNS	NH_4Cl	NH_4Br	NH_4NO_3
0.00	1.25	1.25	1.25	1.25
0.01	0.6	1.7	2.4	1.4
0.05	—	—	5.1	—
0.10	1.0	2.2	12.2	1.6
0.50	3.4	4.5	—	2.2
1.00	6.7	6.8	--	2.9

TABLE 3
Solubility of $Co[Hg(CNS)_4]$ in Solutions of Electrolytes of Various Concentrations at 20°

Concentration of electrolyte (N)	Solubility of $Co[Hg(CNS)_4]$ (mmol/l)		
	KNO_3	K_2SO_4	$K_2[Hg(CNS)_4]$
0.000	1.46	1.46	1.46
0.001	1.49	1.50	—
0.005	1.51	1.55	—
0.010	1.71	1.92	0.120
0.025	1.78	2.25	0.084
0.050	1.90	2.64	0.064
0.100	2.12	3.15	0.050
0.250	—	—	0.057
0.500	2.77	4.12	0.070
1.000	3.05	5.02	0.106

It is known that addition of foreign ions influences the solubility, the effect being the greater the higher the valence of such ions [16].

For the purpose of establishing how the solubility changed with the ionic strength of the solutions and with the nature of the solvent, we determined the solubility of cobalt tetrathiocyanomercuroate in aqueous solutions of a series of electrolytes.

In the first series of experiments we determined the solubility of this salt in solutions of NH_4CNS, NH_4Cl, NH_4Br and NH_4NO_3 of various concentrations at 13.5°. Saturation was attained in these solutions after 2 hours, just as in the case of aqueous solutions of $Co[Hg(CNS)_4]$. Results are given in Table 2. In solutions of these electrolytes at all concentrations, the solubility of cobalt tetrathiocyanomercuroate is higher than in water, with the exception of 0.01 N and 0.1 N NH_4CNS solutions in which the solubility was lower; this anomaly may be due to the influence of the slight excess of monovalent CNS' ion.

The solubility of the salt under investigation depends not only upon the ionic strength of the solution but also upon the character of the electrolyte. Halogen-containing electrolytes raise the solubility of the salt. The highest solubility is observed in solutions of NH_4Br. The increased solubility of $Co[Hg(CNS)_4]$ in solutions of halogen-containing compounds and in 0.5-1.0 N solutions of NH_4CNS is explained by the formation of complex compounds according to the scheme:

$$
\begin{array}{ccc}
Co[Hg(CNS)_4] \rightleftarrows & Co^{\cdot\cdot} + & [Hg(CNS)_4]'' \\
 & + & + \\
 & 4X' & 4X' \\
 & \downarrow\uparrow & \downarrow\uparrow \\
 & [CoX_4]'' & [HgX_4]'' + 4CNS',
\end{array}
$$

where X = CNS', Cl' or Br'.

Similar experiments were undertaken with the objective of determining the solubility of cobalt tetrathiocyanomercuroate in aqueous solutions of KNO_3, K_2SO_4 and $K_2[Hg(CNS)_4]$ at 20° (Table 3). Saturation in these aqueous solutions was attained in 3 hours.

The following conclusions can be drawn from the data of Table 3:

The solubility of cobalt tetrathiocyanomercuroate in solutions of potassium sulfate and nitrate increases with increasing concentration of electrolyte. Solubility in potassium sulfate solutions is higher than in potassium nitrate solutions of the same concentration. The reason is that at identical concentrations the ionic strength in potassium sulfate solution is higher than in potassium nitrate solution.

The total ionic concentration appreciably influences the solubility of the cobalt salt. In 0.1 N solution of $K_2[Hg(CNS)_4]$ a minimum value of solubility is observed. Consequently, in order to achieve more complete precipitation of $Co[Hg(CNS)_4]$ it is necessary to have excess (0.1 N) of potassium or ammonium tetrathiocyanomercuroate. Solubility in the $K_2[Hg(CNS)_4]$ concentration range of 0.01 to 0.1 N falls with increasing concentration of the total ions in solution. The rise in solubility in the interval of 0.1 to 1.0 N $K_2[Hg(CNS)_4]$ may be explained by the rise in ionic strength of the solution.

When salts of cobalt are precipitated with ammonium or potassium tetrathiocyanomercuroate, the solution above the precipitate nearly always contains a slight excess of ions capable of influencing the solubility of the precipitate. Similar equilibria between the solid phase and the electrolyte solution is frequently encountered in practice; it was therefore of interest to investigate the system

$$Co[Hg(CNS)_4] - K_2SO_4 - K_2[Hg(CNS)_4]$$

and to follow the change of solubility of $Co[Hg(CNS)_4]$ as a function of the concentration of one component or the other.

We determined the solubility of $Co[Hg(CNS)_4]$ at 20° in solutions with a constant ionic strength (μ) but with various ratios of components, and also in solutions of various ionic strengths with identical ratios of components (Table 4, Fig. 1).

TABLE 4
Solubility of $Co[Hg(CNS)_4]$ in Solutions of K_2SO_4–$K_2[Hg(CNS)_4]$ with Various Ratios of Components at 20°

Total concentration of components (N)	Solubility of $Co[Hg(CNS)_4]$ (mmol/l): Percent content of $K_2[Hg(CNS)_4]$ in the mixture of both salts				
	20	40	60	80	100
0.01	0.740	0.480	0.210	0.180	0.120
0.10	0.243	0.116	0.090	0.071	0.050
0.50	0.280	0.144	0.095	0.075	0.069

TABLE 5
Activity Coefficients of $Co[Hg(CNS)_4]$ in Dilute Solutions of KNO_3 and K_2SO_4

Concentration of electrolyte (N)	Mean activity coefficients of $Co[Hg(CNS)_4]$ in solutions of	
	KNO_3	K_2SO_4
0.000	0.86	0.86
0.001	0.84	0.83
0.002	0.83	0.81
0.005	0.80	0.73
0.010	0.73	0.66

Curves A_1C_1, A_2C_2, A_3C_3, A_4C_4, A_5C_5 in Fig. 1 show the change of solubility of the salt in pure solutions of $K_2[Hg(CNS)_4]$ and in mixtures of identical percentage content of components. Each of these curves has a minimum at a point with an ionic strength of about 0.15, which corresponds to a total of 0.1 N concentration of the components in the mixtures. This confirms the above suggestion that it is desirable to take a 0.1 N excess of precipitant for precipitation of cobalt tetrathiocyanomercuroate. Curves A_1A_5, B_1B_5 and C_1C_5 show the change of solubility in mixtures with identical ionic strength but differing ratios of components.

With falling percentage content of total ions in the mixtures, the solubility increases. Similar data were obtained also in the case of the system $Co[Hg(CNS)_4] - KNO_3 - K_2[Hg(CNS)_4]$ (Fig. 2).

Fig. 1. Solubility of Co[HgCNS)$_4$]at 20° in solutions of $K_2SO_4-K_2[Hg(CNS)_4]$ with various ratios of components.

Fig. 2. Solubility of $Co[Hg(CNS)_4]$ at 20° in solutions of $KNO_3-K_2[Hg(CNS)_4]$ with various ratios of components.

Some of the data in Table 3 on determination of the solubility of $Co[Hg(CNS)_4]$ in water and in dilute solutions of potassium nitrate and sulfate are plotted in Fig. 3 *. These permitted calculation of the activity product and of the mean activity coefficients of $Co[Hg(CNS)_4]$. As we see from Fig. 3, in the region of approximate conformity with the law of ionic strength, the solubility of cobalt tetrathiocyanomercuroate in solutions of potassium sulfate and nitrate of identical ionic strength is substantially constant.

Solubility in solutions of zero ionic strength, calculated from the graph, is $1.25 \cdot 10^{-3}$ mol/l. Consequently, the activity product $P_a = (1.25 \cdot 10^{-3})^2 \approx 1.5 \cdot 10^{-6}$. Using the values of P_a and S of the salt under investigation, we calculated the mean coefficients of activity (Table 5) according to the formula: $f = \sqrt{Pa/S^2}$.

With increasing ionic strength of solution the activity coefficients decrease.

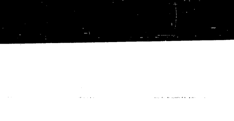

Fig. 3. Solubility of $Co[Hg(CNS)_4]$ in dilute solutions of KNO_3 and K_2SO_4.

SUMMARY

1. The solubility of $Co[Hg(CNS)_4]$ in water was determined as a function of the temperature.

2. The solubility of $Co[Hg(CNS)_4]$ was determined in solutions of a series of electrolytes at 13.5 and 20°. The solubility of this salt was shown to be dependent upon the ionic strength of the solutions, and upon the nature and ratios of amounts of salts present in the solvent.

Halogen-containing electrolytes considerably increase the solubility due to complex formation. In presence of monovalent ions the solubility is considerably lower than in water. Optimum conditions were found for precipitation of cobalt by a solution of ammonium tetrathiocyanomercuroate.

3. Calculation of the activity product of $Co[Hg(CNS)_4]$, gave a value of $1.5 \cdot 10^{-6}$; the mean activity coefficients of this salt in aqueous solutions of potassium nitrate and sulfate were also calculated.

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STRATIFICATION IN TERNARY SYSTEMS WHEN THE COMPONENT BINARY SYSTEMS ARE HOMOGENEOUS

I. L. Krupatkin

The problem of the development of layering in ternary systems whose component binaries are all homogeneous was raised long ago in the literature [1]. The system water-phenol-acetone with an upper ternary critical point has been cited [2] as an example of such a case. In isothermal sections of this system, existing at temperatures above the critical binary layering system water-phenol but below the ternary critical point, a layering region exists when all the binary systems are homogeneous at these temperatures. On lowering the temperature, however, the layering isotherms are concentrically widened and reach the side of the system water-phenol, and then layering is developed in the latter. Consequently, the regions of layering of the ternary and binary system overlap and therefore the system water-phenol-acetone does not belong to the type of ternary systems under consideration.

Nevertheless it is possible in principle to develop layering in a ternary system when layering is entirely absent from any given pair of the components at any temperatures. The objective of the present investigation was to investigate such a case, to elucidate the causes of layer formation and to establish the conditions for prognosis of ternary systems of the types in question. The system selected for this investigation was antipyrine-chloral hydrate-water.

EXPERIMENTAL

The following substances were used: chloral hydrate (pharmacopeial) with m.p. 48°; antipyrine (pharmacopeial) with m.p. 113°; and water, twice distilled. The binary systems entering into the three-component system have the following characteristics:

System chloral hydrate – antipyrine (X – A) was investigated by the fusion method [3]. It was found to contain two compounds with nearly identical melting point; Compound X_2A melts at 61.8° and contains 36.30% antipyrine; Compound XA melts at 62.3° and contains 53.30% antipyrine. The system chloral hydrate – antipyrine predominates in the system chloral hydrate – antipyrine – water.

The system chloral hydrate – water was studied in the course of investigation of the binary system chloral – water by the fusion [4] and viscosity [5] methods. The fusion curves of the system chloral – water revealed the presence of 3 compounds in which 1 molecule of chloral was associated with respectively $\frac{1}{2}$, 1 and 7 molecules of water. Consequently in the system chloral hydrate – water the fusion diagram recorded one compound – the heptahydrate (melting at –1.4°). But on the viscosity curves of the system chloral – water, already at 50° only one compound is reflected – chloral hydrate. Thus, in the liquid phase of the system chloral hydrate – water, neither the heptahydrate nor other compounds are detected. In the system chloral – water the mixture containing 40-60 mol-% chloral stratifies on heating to 175-190° [6]; hence at lower temperatures, at which stratification occurs in the ternary system, the system chloral hydrate – water is close to the stratification point, i.e. it is in a latent stratified state [8].

The system antipyrine – water was studied in the present work. The solubility of antipyrine in water was determined visually. The data obtained are presented in Table 1 and plotted in Fig. 1. The diagram shows that the crystallization curve of antipyrine has a nearly horizontal portion at a temperature of about 80° over the stretch of 30 to 70% antipyrine, which is characteristic of systems with metastable layering [7] or of systems existing in the latent-layering state [8]. An attempt was therefore made to detect layering. With this objective, three mixtures, containing 30, 50 and 70% antipyrine were heated to 160° and undercooled to 70° below their recrystallization temperatures, i.e., to 10°; in no case, however, was layering manifested. Consequently, it had been demonstrated that the system antipyrine – water is a system of the latent-layering type.

TABLE 1
Equilibrium in the System Antipyrine – Water

Water content (in weight %)	Crystallization temp.	Water content (in weight %)	Crystallization temp.
0.00	113.0°	50.00	81.0°
10.00	98.0	60.00	80.5
20.00	88.5	70.00	79.0
30.00	83.0	80.00	69.0
40.00	82.0		

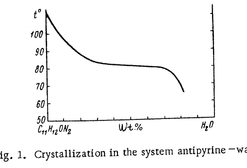

Fig. 1. Crystallization in the system antipyrine – water.

Ternary system antipyrine – chloral hydrate – water. This was investigated by the stratification method of V.F. Alekseev [9]. The boundaries of the stratification region were established by study of the polythermic sections of the prism of the ternary system, extending from the water edge to the boundary of the system antipyrine – chloral hydrate. Five cuts with 25.0, 36.3, 45.0, 53.3 and 65.0% antipyrine were investigated. The data so obtained are collected in Table 2, and the stratification polytherm is plotted in Fig. 2 in which the numbers designating the polytherms increase with increasing percentage of antipyrine in the cuts. The cuts containing 36.3 and 53.3% antipyrine pass through the compositions of the compounds of the system antipyrine – chloral hydrate. Fig. 2 shows that in nearly all the cuts the solubility of the liquid mixtures of antipyrine with chloral hydrate in water is approximately the same and amounts to about 20% of the mixtures. Only in Cut V does it reach 30%. Conversely, the solubility of water in the indicated mixtures varies considerably, changing from 25% water in Cut IV to 65% in Cut I. In all the cuts, apart from the left branch of the second polytherm, rise of temperature does not significantly change the reciprocal solubility of the liquids; therefore the solubility curves are nearly vertical. On the other hand, in the vicinity of the temperature of complete mis cibility of the liquids, the solubility depends markedly upon the temperature; hence the maxima of the polytherms are very flat, and the polytherms acquire a certain angularity. These maxima rise from Cut I to Cut IV and then start to fall; Cut IV is therefore the highest cut of the system. A critical line can be drawn through the maximum points of the polytherms. Its projection on to the triangle of composition is represented in Fig. 3, Curve 1,K,2. It has a turning point K on the cut corresponding to the system antipyrine – chloral hydrate on the composition of compound XA. Therefore the critical line reflects the formation of a compound in the predominant system.

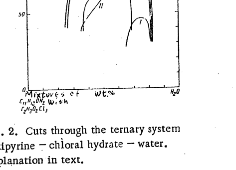

Fig. 2. Cuts through the ternary system antipyrine – chloral hydrate – water. Explanation in text.

TABLE 2
Polytherms of the System Antipyrine – Chloral Hydrate – Water

Cut I 25%, 75%*		Cut II 36.3%, 63.7%*		Cut III 45%, 55%*		Cut IV 53.3%, 46.7%*		Cut V 65%, 35%*	
a	b	a	b	a	b	a	b	a	b
56.11	31.0°	36.56	43.0°	27.23	45.0°	24.99	42.0°	36.77	40.0°
58.00	39.0	45.00	53.5	28.97	62.0	27.00	60.0	40.00	59.0
70.72	45.0	55.00	65.5	32.00	72.0	29.58	69.0	50.20	66.0
75.00	46.0	64.89	74.0	40.00	79.0	38.75	82.0	60.00	68.0
78.70	44.5	70.00	76.0	51.53	82.5	50.00	86.0	65.00	68.5
80.51	39.0	75.10	76.5	63.13	85.0	60.00	87.5	67.08	65.0
		77.52	74.0	70.00	84.5	70.00	86.0	69.14	43.0
		80.00	63.0	75.28	83.0	75.31	84.0		
		81.50	38.0	80.00	69.0	80.00	75.0		
				82.07	39.0	82.13	58.0		
						82.50	35.0		

Note: a) Water content (in wt. %); b) stratification temp.; * % antipyrene, % chloral hydrate

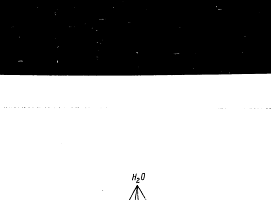

Fig. 3. Solubility isotherms of the ternary system antipyrine – chloral hydrate – water. Explanation in text.

From the plotted polytherms were constructed 4 solubility isotherms of the system antipyrine – chloral hydrate – water at temperatures of 45, 60, 70 and 80° (Fig. 3); they constitute closed concentric curves, diminishing in size with rising temperature. In this three-component system, we consequently have an upper ternary critical point K corresponding to 21.3% antipyrine, 18.7% chloral hydrate and 60.0% water and a temperature of 88°. It coincides with the inflection of the critical line and is located in the cut corresponding to the system antipyrine – chloral hydrate on the composition of Compound XA. All the isotherms have minima of reciprocal solubility of the liquid phases which occur in the same cut on the compound of Composition XA; it is thus confirmed that the latter exists in the liquid phase of the system. The compound of composition X_2A is not reflected on the stratification isotherms.

It was observed above that in all the polythermal cuts the stratification curves are nearly vertical. With falling temperature they do not approach any of the boundaries of the components of the binary systems, since the latter are then homogeneous. Consequently, the surface of stratification of the ternary system is not associated with an upper region of stratification of the system chloral hydrate – water. The temperature interval between them is high – of the order of 100°. Hence, the region of stratification of the ternary system is not a continuation of the region of stable stratification of the components of the binary systems.

The surface of stratification of the ternary system might have been developed as a continuation of the plane of metastable stratification of the component binary systems as a case of transition of the metastable equilibrium between the liquid phases and the stable phase. A similar transition was also realized [10], and in the present ternary system it could be suggested that it proceeds from the boundary of the system antipyrine – water, since the slope of its crystallization curve could be governed by the existence of metastable stratification in this system. However, as described above, this stratification was not detected; this route to the development of stratification in the present system does not exist.

One of the causes of development of stratification in a ternary system with homogeneous boundaries is the formation of a chemical compound (or complex) which is present in the liquid phase in its predominating binary system. This condition is essential but is not in itself sufficient. The interrelations of the predominating system with the third component may be such that the latter and the chemical compound have unlimited solubility in one another, in which event stratification does not occur in the ternary system when its binary systems are homogeneous. This is observed, for example, in the homogeneous system allyl mustard oil – aniline – toluene, which was investigated by N. S. Kurnakov and I. K. Kvyat [11]. In this case in the predominating system allyl mustard oil – aniline the compound allylphenylthiourea is formed which has unlimited solubility in toluene; hence the second cause of development of stratification in ternary systems of the type considered is a character of its interrelations with the predominating system containing the third component, such that the compound formed and the third component have limited solubility in one another.

The limited solubility of the compound of the predominating system depends upon the properties of the compound and the solvent. It is closely bound up with the character of the interaction of the solvent with the predominating system, and consequently it also depends upon the character of the remaining two subsidiary binary systems. If the systems (containing one component in common) are close to stratification, then the strong mutual reaction of their second components leads to weakening of the interaction in the subsidiary systems and mixtures of the reacting binary system with the third component. Moreover, in proportion to increasing intensification

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of interaction in mixtures of the predominating system, the reaction is weakened between those mixtures and the third component. This process of progressive weakening of the bond proceeds from the planes of the binary subsidiary systems inside the prism of the ternary system and leads within it to such an interaction between the compound of the reacting binary system (and mixtures close to it) and the solvent that they have limited mutual solubility. Consequently, the development of a region of stratification in a ternary system containing homogeneous binary systems is governed by the behavior of the subsidiary, latently stratified systems as stratifying systems (which was previously observed [8]) and by interaction throughout the whole ternary system.

The above-described scheme of the phenomenon is not universal, but it is confirmed as one of the schemes in the system antipyrine – chloral hydrate – water. Its subsidiary systems antipyrine – water and chloral hydrate – water are close to the stratification point (the latter at the temperatures of stratification in the ternay system), while in the predominant system antipyrine – chloral hydrate a compound of the Composition XA is formed which is present in the liquid phase. Compound XA and water have limited mutual solubility.

Certain conditions for prognosis of ternary systems, in which stratification occurs while the component binary systems are homogeneous, follow from the above considerations. The first requirement is that a compound (or complex) should be formed in the predominating system of the particular ternary system: secondly, one or two of the binary subsidiary systems should show symptoms of latent stratification (for example, nearly horizontal lengths on the crystallization curves). When these conditions are satisfied, we can expect the development of stratification in ternary systems, where binary component systems are homogeneous. The paper recently published by E. F. Zhuravlev with a similar theme [12] does not conflict with the data of the present paper.

SUMMARY

1. A study was made of crystallization in the system antipyrine – water, and a large, nearly horizontal length was observed on the crystallization curve of antipyrine. No stratification was observed in it either in the stable or metastable state.

2. A study was made of the equilibrium of the liquid phases in the ternary system antipyrine – chloral hydrate – water; within the prism of this system was detected a region of stratification with an upper ternary critical point while the component binary systems were homogeneous.

3. The causes were established of the development of stratification in ternary systems with homogeneous binaries, and some conditions for prognosis of such ternary systems were formulated.

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PHYSICO-CHEMICAL INVESTIGATION OF SYSTEMS CONTAINING DIOXANE

VIII. THE SYSTEM SULFURIC ACID - DIOXANE

Ya. F. Mezhenny

In our previous papers we described the results of investigations of dioxane solutions of aluminum bromide [1], sulfur trioxide [2], pyrosulfuric acid [3], phosphorous acid [4], and hydrogen chloride [5, 6]. In the present paper we consider the system sulfuric acid - dioxane.

A. E. Favorsky [7] had already established that on reaction of sulfuric acid with dioxane the dioxanate of sulfuric acid is formed. A. E. Favorsky isolated this compound and determined its composition and melting point. As far as we know, however, the fusion diagram of the system dioxane - sulfuric acid has never been studied. The starting substances in the present investigation were dioxane with m.p. 10.7° and sulfuric acid with m.p. 10.6°.

Thermal analysis of the system sulfuric acid - dioxane. As we see from the diagram, the fusion curve descends to 69 mol-% H_2SO_4. Its further plotting had to be abandoned due to the considerable experimental difficulties associated with rising viscosity and change of color to brown. The diagram clearly indicates the existence of only one compound of dioxane with sulfuric acid, corresponding to the composition $H_2SO_4 \cdot C_4H_8O_2$. A compound of the same composition was established by an entirely different method by A. E. Favorsky [7]. The melting point of this compound on our fusion diagram is 100-101°. Favorsky reports a melting point of 101° for his compound. We also established a eutectic point on the diagram corresponding to 14 mol-% sulfuric acid with a crystallization temperature of approximately 5°.

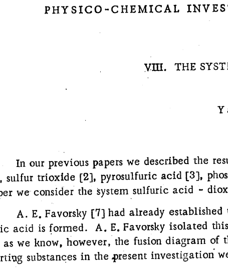

Diagram. System sulfuric acid - dioxane. I) Melting point, II) specific electrical conductivity.

Electrical conductivity of the system sulfuric acid - dioxane. Measurements were made with addition of dioxane to pure sulfuric acid as well as of sulfuric acid to dioxane. Due to the circumstance that over a wide concentration interval at room temperature the system dioxane - sulfuric acid is in the solid state, it was necessary to deviate rather widely from the previously selected temperature conditions. The sulfuric acid at 25° had the specific electrical conductivity $\varkappa = 1.64 \cdot 10^{-2}$. According to the measurements of M. Usanovich [8, 9] the specific electrical conductivity of the acid at 25° is $1.17 \cdot 10^{-2}$ *. We see from the diagram that sulfuric acid in dioxane at low and even quite high concentrations has a relatively low specific electrical conductivity with a maximum shifted toward the sulfuric acid, i.e. into the region of dilute solution of the compound $H_2SO_4 \cdot C_4H_8O_2$ in sulfuric acid.

Our results for the electrical conductivity of

* With variations between $0.9 \cdot 10^{-2}$ and $1.5 \cdot 10^{-2}$.

solutions of sulfuric acid in dioxane, converted to equivalent electrical conductivity, are given in Table 1.

Table 1
Equivalent Electrical Conductivity (λ) of Solutions of Sulfuric Acid in Dioxane

Temperature	Concentration (g-equiv./liter)	λ
60°	36.20	3.74
25	36.20	1.422
25	28.02	0.796
20	2.48	0.0238

TABLE 2
Cryoscopic Investigation of the System Sulfuric Acid-Dioxane. (Dioxane sample G = 6.629 g)

Weight of sulfuric acid (g) in g	Δt	$M=4.83\frac{1000g}{\Delta t \cdot G}$
0.7394	4.20	135
0.9943	6.20	118

We see from the data of Table 1 that within the sulfuric acid concentration range of 36 to 2.48 g-equiv./l, the values of λ are between 3.74 and 0.0238, the values falling steeply with dilution. At a concentration of 1.1 g-equiv./l the value of λ is of the order of only 10^{-3}. Consequently, sulfuric acid in dioxane is a weaker electrolyte than acetic acid in water, since at a concentration in water of 1 g-equiv./l, the λ of acetic acid=1.32.

Cryoscopy of sulfuric acid in dioxane. Measurement of the electrical conductivity of dilute solutions of sulfuric acid in dioxane does not give grounds for classifying it either as a strong or weak electrolyte. This conclusion was checked by cryoscopic measurements of solutions of sulfuric acid in dioxane, results of which appear in Table 2.

These data show that cryoscopy likewise does not indicate the existence of simple ions of sulfuric acid.

SUMMARY

1. One point corresponding to the complex compound $H_2SO_4 \cdot C_4H_8O_2$ with m.p. approx. 100° was found from the fusion diagram of the system dioxane-sulfuric acid.

2. The specific electrical conductivity of this system is insignificant at low concentrations of sulfuric acid, and it rises with increasing relative amount of sulfuric acid. The curve of composition versus κ of this system has a maximum which is very strongly displaced in the direction of sulfuric acid and falls steeply on transition to pure sulfuric acid.

3. The molecular weight of sulfuric acid in dioxane determined by the cryoscopic method is higher than that theoretically expected.

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INVESTIGATION OF COMPLEX FORMATION IN THE SYSTEM ALUMINUM CHLORIDE - UREA - WATER BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

B. Ya. Rabinovich *

Crystallization from aqueous solutions gives complex compounds of some trivalent metals with urea whose composition corresponds to the general formula $[Me(CON_2H_4)_6]X_3$. This type of compound has been described [1] in the case of aluminum iodide, perchlorate, permanganate and dichromate. Compounds of aluminum chloride and bromide with urea are unknown.

With the objective of clarifying the molecular state of urea complexes of aluminum in aqueous solution and of establishing whether a uminum chloride forms a complex with urea, we studied this system by the method of physico-chemical analysis, and determined the density, viscosity and specific electrical conductivity of the solutions at 15 and 25°.

J. Ostromislensky's technique [2] of isomolar concentrations was applied. Semimolar solutions of aluminum chloride hexahydrate and urea were stirred in various proportions by volume but with constant total volume. The measurement technique has been described in one of our earlier papers [3].

DISCUSSION OF RESULTS

Results of measurements of density and viscosity are plotted in Fig. 1. The viscosity changes linearly with the composition of the system. In the region of low concentrations of urea the viscosity isotherms have a very slight convexity toward the axis of composition; like the density isotherms, however, they supply no evidence of chemical interaction between the components of the system. The temperature coefficient of viscosity, calculated from the formula $\frac{\eta^{15}-\eta^{25}}{\eta^{15}\cdot 10}$, is 0.021 and does not change with the concentration of urea in the system. Results of measurements of specific electrical conductivity are plotted in Fig. 2. The specific electrical conductivity isotherms have a discontinuity at an $AlCl_3:CO(NH_2)_2$ molar ratio of 1:1. The temperature coefficient of electrical conductivity, calculated from the formula $\frac{\kappa^{25}-\kappa^{15}}{\kappa^{15}\cdot 10}$ has a very weak minimum at the same ratio of components.

Consequently, only the specific electrical conductivity isotherms give some indication of the occurrence of complex formation in the system. The absence of characteristic points on the viscosity isotherms is evidently due to the very low concentrations of the solutions [4]. The solutions that we investigated had a maximum aluminum chloride concentration of 6.3%, and a maximum urea concentration of 3%. Both the aluminum chloride and its complex mixture were dissociated to a considerable extent in these solutions. In these circumstances it is possible that the existence of the complex was not reflected on the viscosity isotherms.

Aluminum manifests a great chemical similarity to chromium in the trivalent state. This is reflected in the properties of complex compounds of aluminum and trivalent chromium with urea. In the crystalline state they have identical compositions and are probably isomorphous. These complexes break down in aqueous solution, the urea molecules being replaced in the inner coordination shell by water molecules. According to the data of K. B. Yatsimirsky and E. I. Yasinskene [5], who examined the absorption spectra of solutions of aluminum chloride and urea, the $[Cr(CON_2H_4)(H_2O)_5]$ ion is formed in aqueous solution. We obtained analogous results for aluminum chloride by measuring the specific electrical conductivity. As Taube showed [6], the difference is that decomposition of complex compounds of aluminum proceeds very quickly whereas the decomposition of chromium compounds

* Deceased.

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proceeds relatively slowly. The analogy in properties extends also to other compounds of aluminum and chromium, in particular to the complex oxalates. The inference is that in the similar complex compounds of aluminum and chromium the character of the bond between complex former and addends is identical, regardless of the different electronic structures of the Al^{3+} and Cr^{3+} ions. It is therefore impossible to accept as fully justified that classification of complex character and of the nature of the bond in the complex compounds which assumes that there are differences in the structure of the outer electron shells of the complex formers.

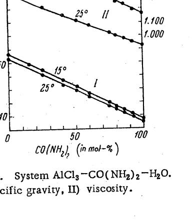

Fig. 1. System $AlCl_3-CO(NH_2)_2-H_2O$. I) Specific gravity, II) viscosity.

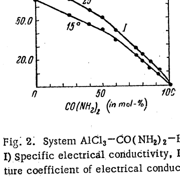

Fig. 2. System $AlCl_3-CO(NH_2)_2-H_2O$. I) Specific electrical conductivity, II) temperature coefficient of electrical conductivity.

SUMMARY

1. The density, viscosity and specific electrical conductivity of the system aluminum chloride - urea - water at 15 and 25° were measured by the method involving use of isomolar concentrations.

2. The density changes linearly with the composition of the system.

In the region of low concentrations of urea the viscosity isotherms are slightly convex to the axis of composition. The temperature coefficient of viscosity is constant and does not vary with the composition of the system.

3. The specific electrical conductivity isotherms have a discontinuity at the molar ratio $AlCl_3 : CO(NH_2)_2 = 1 : 1$. The temperature coefficient of electrical conductivity has a weak minimum at the same point.

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CAMPHORATES OF SOME RARE EARTH ELEMENTS

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Of the very large number of salts of rare earth elements with organic acids, only a few are known in which the acids might be optically active. Although some of them (such as tartrates) have found application in chemical laboratory courses, very little study has been devoted to their salts. This is true of their relative solubility and complex-forming tendency, not to mention their optical properties.

One of us previously synthesized α-bromo-d-camphor-p-sulfonates of lanthanum, cerium and neodymium and showed the possibility of utilizing their optical properties for evaluation of their purity on the basis of the specific rotation of solutions of the salts [1]. Our attention was attracted by the little studied d-camphorates of elements of the cerium group which Coniglio [2] synthesized by precipitation with d-camphoric acid of the acetates of these elements (acidified with acetic acid). Cerium camphorate has been described as insoluble in water [3].

Our experiments on preparation of the d-camphorates of elements of the cerium group indicated that they were moderately soluble in water. Due to the fact that solutions of the salts could be prepared with concentrations of only 1-2%, we have refrained up to now from applying the values of their optical activity to evaluation of the purity of the preparations. In the course of the work, however, it was established that the d-camphorates of the elements of the cerium group nevertheless differ appreciably from one another in respect to solubility.

EXPERIMENTAL

To prepare the camphorates of the rare-earth elements, we used the chlorides of lanthanum, cerium, praseodymium and neodymium, solutions of which were prepared by treatment of weighed portions of the carbonates $E_2(CO_3)_3 \cdot nH_2O$ with 20% hydrochloric acid, allowing for a slight excess of undissolved carbonate. A solution of an equivalent quantity of sodium camphorate (calculated on 3 moles sodium camphorate to 2 moles of the initial carbonate of the rare-earth element) was added drop-wise to the solution obtained after the carbonate residue was filtered off. As the solution was added, a voluminous amorphous precipitate of d-camphorate came down, colorless in the case of lanthanum, light yellow – in the case of cerium, pinkish – neodymium and faintly green – praseodymium. The residues were filtered off, washed with distilled water and dried in a vacuum-desiccator over calcium chloride and phosphoric anhydride. The dry camphorates of the rare earth elements were in the form of powders which did not melt when heated to 300°.

At 20°, the salts visibly dissolved in water. Solutions were prepared with a 2% content of lanthanum camphorate, cerium camphorate, praseodymium and neodymium camphorates; lanthanum and cerium camphorates partially precipitated soon after dissolving, but praseodymium and neodymium camphorates stayed in solution for several days and then began to precipitate in negligible amounts. Upon slight heating over a water bath (30-35°), voluminous precipitates of the camphorates of the corresponding rare earth elements came down; they dissolved upon cooling to 1-2°.

The camphorates of the rare-earth elements were practically insoluble in organic solvents (methyl and ethyl alcohols, chloroform, acetone, ether, benzene and others).

Determination of the content of rare earth metal (in the form of oxide) in the d-camphorates was performed by simple calcining of a weighed sample of the salt (dried to constant weight) in a crucible furnace. Heating was at first carried out with care, in a covered crucible in order to avoid loss of material which might occur upon rapid combustion of the organic portion. The crucible cover was then removed and calcination was continued at 700-800°. After 3-4 hours of calcining, the constant weight of the metal oxide was determined.

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d-Camphorate of lanthanum: Found %: La 31.37. $La_2(C_{10}H_{14}O_4)_3$. Calculated %: La 31.84.

d-Camphorate of cerium: Found %: Ce 31.96. $Ce_2(C_{10}H_{14}O_4)_3$. Calculated %: Ce 32.03.

d-Camphorate of neodymium: Found %: Nd 29.82. $Nd_2(C_{10}H_{14}O_4)_3$. Calculated %: Nd 32.67.

Praseodymium camphorate was not analyzed, since according to our data, the oxide resulting upon calcination of the salt of praseodymium with volatile acids, does not always correspond to the exact composition Pr_6O_{11}.

Upon separation of neodymium camphorate by heating its aqueous solution, after removal of the precipitate, the filtrate remained pink. When an additional quantity of the salt was separated, superheating was allowed (above 50°). The precipitate which now came down had a less intense pink color and upon cooling, almost did not dissolve at all in the water. The salt was filtered off and dried in a vacuum-desiccator to constant weight. The analytical results corroborated our supposition of the presence of hydrolysis with formation of the basic salt upon heating. After separation of the precipitate of basic salt, the filtrate was placed in a desiccator over sulfuric acid. After some time, colorless crystals (0.1 g) separated out, which investigation proved to be free d-camphoric acid, poorly soluble in water, m.p. 187°. Upon separation of neodymium d-camphorate from the solution, heating carefully to avoid hydrolysis, it proved convenient to precipitate it by addition of 96% ethyl alcohol; neodymium camphorate quantitatively came down as a precipitate.

Basic d-camphorate of neodymium. Found %: Nd 24.56. $Nd_2(OH)_2(C_{10}H_{14}O_4)_2$. Calculated %: Nd 24.89.

The hydrolysis of the salt may be represented by the following equation:

$$Nd_2(C_{10}H_{14}O_4)_3 + 2H_2O = Nd_2(OH)_2(C_{10}H_{14}O_4)_2 + C_{10}H_{16}O_4 .$$

The slightly low content of neodymium in the d-camphorate (29.82%) in comparison to the calculated (32.67%) may be explained by the presence of slight amounts of the basic salt in the latter compound.

d-Camphorate of neodymium, calculated from ethyl alcohol solution. Found %: Nd 32.38. $Nd_2(C_{10}H_{14}O_4)_3$. Calculated %: Nd 32.67.

We also prepared thorium camphorate, which was less soluble than the corresponding lanthanum salt.

SUMMARY

1. A method is proposed for preparation of d-camphorates of lanthanum, cerium, praseodymium and neodymium by double decomposition of aqueous solutions of their chlorides with sodium camphorate.

2. It was established that, contrary to the literature data, the d-camphorates of the elements of the cerium group are moderately soluble in water; their solubility falls in the order Nd, Pr, Ce, La and Th; the solubility of the d-camphorates of the rare earth elements increases with cooling and decreases on heating.

3. d-Camphorates of the rare earth elements are susceptible to hydrolysis, and the possibility was shown of separating them from aqueous solutions (with avoidance of hydrolysis) by precipitation with ethyl alcohol.

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DOUBLE SALTS OF LANTHANUM, CERIUM, PRASEODYMIUM AND NEODYMIUM WITH TRIPHENYLBENZYLPHOSPHONIUM NITRATE

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As shown earlier [1], tetraphenylphosphonium nitrate [2] is capable of forming double salts with nitrates of the rare earth elements; these double salts break down to the original components under the action of water and vary considerably in their solubility in 96% ethyl alcohol or its mixture with chloroform. In view of this behavior, it was not without interest to prepare similar double salts but using as the organic component triphenylbenzylphosphonium nitrate, the latter being more easily accessible, and to study the properties of such double salts.

It was found that the double salts of lanthanum, cerium, praseodymium and neodymium with triphenylbenzylphosphonium nitrate have a composition and structure corresponding to the general formula $[(C_6H_5)_3(C_6H_5CH_2)P]_2[E(NO_3)_5]$, where E is an atom of a rare-earth element. In harmony with such a structure, the alcoholic or alcohol-chloroformic solutions of these double nitrates possess a high electrical conductivity. The most soluble compound is the double lanthanum triphenylbenzylphosphonium nitrate; the least soluble is the neodymium salt. The solubility of these salts was higher than that of the corresponding tetraphenylphosphonium double nitrates. Of special interest is the very wide difference in solubility of the double salts of elements with such similar properties as praseodymium and neodymium; the double salts of the latter also crystallize well.

EXPERIMENTAL

Double nitrate of lanthanum and triphenylbenzylphosphonium. Triphenylbenzylphosphonium nitrate was prepared from triphenylbenzylphosphonium chloride, prepared by reacting triphenylphosphine [3] with benzyl chloride [4]. 1.06 g of triphenylbenzylphosphonium nitrate was added to a solution of 0.68 g $La(NO_3)_3 \cdot 6H_2O$ in 2 ml of 96% ethyl alcohol and the mixture was heated until the tetrasubstituted phosphonium salt dissolved. The colorless crystals which separated out upon cooling, were filtered off under reduced pressure and washed three times with chloroform (3 ml). The crude product (1.37 g), m.p. 158-158.5°, was recrystallized from 96% alcohol. Yield 1.21 g (69%) m.p. 158.5°.

Found %: C 51.87; H 3.89; La 11.98. $C_{50}H_{44}O_{15}N_5P_2La$. Calculated %: C 51.93; H 3.84; La 12.02.

The double nitrate of lanthanum and triphenylbenzylphosphonium formed colorless crystals, very readily soluble in 96% ethyl alcohol, especially in hot alcohol, and in its mixture with chloroform. It was practically insoluble in ethyl alcohol and in hydrocarbons. It was decomposed by water into its components in the same manner as similar salts of other rare earth elements.

Double nitrate of cerium and triphenylbenzylphosphonium. 2.27 g of triphenylbenzylphosphonium nitrate was added to a solution of 1.04 g of $Ce(NO_3)_3 \cdot 3H_2O$ (of analytical grade with admixture of Dy salts) in 4 ml of ethyl alcohol. The mixture was heated over a water bath until the salt dissolved. The crystals which separated out (2.68 g), after the solution had stood for a long period, were filtered off and washed with 2 ml of ethyl alcohol. From the mother liquor we isolated 0.21 g more of the double salt. Two-fold recrystallization of the crude product from ethyl alcohol yielded colorless crystals (2.17 g) in the form of plates, m.p. 160.75°

Found %: C 51.81; H 3.86; Ce 12.07. $C_{50}H_{44}O_{15}N_5P_2Ce$. Calculated %: C 51.88; H 3.83; Ce 12.12.

The double nitrate of cerium and triphenylbenzylphosphonium was readily soluble in ethyl alcohol, especially upon heating, in acetone and in alcohol-chloroform mixture. It was practically insoluble in chloroform, ethyl ether, benzene, toluene and xylene. Addition of water to its alcoholic solution caused it to decompose into its components.

Double nitrate of praseodymium and triphenylbenzylphosphonium. 1.64 g of triphenylbenzylphosphonium nitrate was added to a solution of 0.86 g of $Pr(NO_3)_3 \cdot 6H_2O$ in 3 ml of 96% ethyl alcohol. From the yellowish-green solution obtained upon heating on a water bath, part of the solvent was driven off. Light-green crystals separated out upon slow cooling of the solution, weight 1.85 g after treatment. From the mother liquor we isolated 0.17 g more of the less pure double salt. The crude product was recrystallized from boiling ethyl alcohol. Yield 1.48 g, m.p. 162.5°.

Found %: C 51.80; H 3.89; N 6.02. $C_{50}H_{44}O_{15}N_5P_2Pr$. Calculated %: C 51.85; H 3.83; N 6.05.

The double nitrate of praseodymium and triphenylbenzylphosphonium was readily soluble in boiling ethyl alcohol, less however, than the corresponding cerium salt, and was also readily soluble in acetone. It was practically insoluble in ethyl ether, chloroform and hydrocarbons. It was decomposed by water in the manner of the above described cerium salt.

Double nitrate of neodymium and triphenylbenzylphosphonium. 1.67 g of triphenylbenzylphosphonium nitrate was added to a solution of 0.88 g of $Nd(NO_3)_3 \cdot 6H_2O$ in 5 ml of hot 96% ethyl alcohol and the mixture was then heated on a water bath, part of the solvent was driven off and upon cooling, the product crystallized. The lilac-colored crystals that separated out weighed 2.32 g after treatment and were recrystallized from 5.8 ml of boiling ethyl alcohol. Yield of pure product was 2.17 g, m.p. 164.5°. From the mother liquor we isolated 0.15 g more of the less pure double salt.

Found %: C 51.67; H 3.85; Nd 12.38. $C_{50}H_{44}O_{15}N_5P_2Nd$. Calculated %: C 51.70; H 3.82; Nd 12.43.

The double nitrate of neodymium and triphenylbenzylphosphonium was appreciably less soluble than the preceding praseodymium salt in cold, and especially in boiling, ethyl alcohol (in 1 part by weight of the latter, 2.23 parts by weight of the praseodymium salt and only 0.57 part by weight of the neodymium salt dissolved). It was readily soluble in methanol and acetone. It was very sparingly soluble in cold isoamyl alcohol, more readily soluble in hot. It was practically insoluble in ethyl ether, chloroform and hydrocarbons. Upon solution in water, it underwent hydrolysis.

SUMMARY

1. Double salts of lanthanum, cerium, praseodymium and neodymium with triphenylbenzylphosphonium nitrate were prepared and described.

2. A considerable difference was found between the solubilities of the prepared salts of praseodymium and neodymium.

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INNER COMPLEX SALTS OF AZO COMPOUNDS

III. REACTION OF COPPER SALTS WITH SOME o-HYDROXY- AND o-AMINO, o'-ALKOXY- AND -o'-AROXY-MONOAZO COMPOUNDS

V. I. Mur

The preparation was recently announced [1] of complexes of copper with o-hydroxy- and o-amino-o'-methoxyazo compounds in 1:1 ratio. On the basis of some of their properties, of their elementary analyses and of the absence of similar compounds of o-hydroxy- and o-amino-o'-chloro- and -o'-nitro derivatives, they were assigned the following structure:

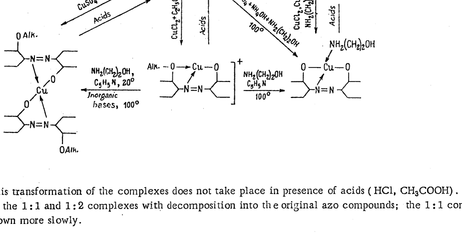
This structure suggests the participation in complex formation of the oxygen of the methoxyl group, acting as a donor in the formation of the complex bond with copper. For confirmation of this supposition and of the belief that the formation of such compounds is not specific merely for the methoxyl group, a study has been made of the reaction of o-hydroxy- and of o-amino-o'-ethoxy- and -o'-phenoxyazo compounds with copper salts.

It was found that under appropriate conditions these ethoxy compounds react with copper chloride to form complexes similar to those obtained from the methoxy derivatives. The molecular weight of these complexes, like those of the 1:1 complexes of the methoxy derivatives, correspond to a monomeric structure.

This confirms the above-mentioned structure of copper complexes of o-hydroxy- and o-amino-o'-methoxyazo compounds and allows us to assign a similar structure to the copper complexes of other alkoxy derivatives of 1:1 composition.

o-Hydroxy- and o-amino-o'-phenoxyazo compounds do not form 1:1 complexes with copper. On reacting them with copper chloride under other conditions, 1:2 complexes are formed [1], identical with those formed on reaction of the same azo compounds with copper tetrammine sulfate. The inability of these phenoxyazo compounds to form 1:1 complexes is evidently due to influence of phenyl which repels the unshared electron pair from the oxygen, thereby excluding the possibility of formation of a complex bond between the oxygen of the phenoxy group and copper. It seemed likely that the introduction of an electron-donating substituent in the o- or p-position of the benzene ring of the phenoxy group might create conditions favorable for formation of 1:1 complexes. On reaction, however, of the azo compound prepared from the diazo compound of o-amino-o'-methoxydiphenyl ether and β-naphthol with copper chloride under the conditions of formation of a 1:1 complex, a 1:2 complex is obtained. The donor properties of the methoxyl group are evidently inadequate for suppression of the acceptor effect of the aromatic nucleus.

Reaction of o-hydroxy- and o-amino-o'-aroxyazo compounds with copper chloride is accompanied by development of a deep color in the reaction solutions. A similar phenomenon is encountered in all the other cases of formation of 1:2 complexes that we examined. The observed increase of intensity of color of the reaction solutions does not correspond to the color change that should have occurred on simple mixing of the differently colored starting solutions. Nor is this color change apparently due to the formation of supersaturated solutions of the complexes; the latter are very poorly soluble in the solvent employed (alcohol) and do not go into solution either when heated under the experimental conditions or under conditions more favorable to their solution. In the light of these facts, it may be suggested that formation of 1:2 complexes is preceded by formation of an intermediate compound (possibly a complex ion; its nature is still obscure). It is interesting that the transformation into 1:2 complexes which is characteristic of 1:1 complexes of copper with o-hydroxy- and o-amino-o'-alkoxyazo compounds is also apparently accompanied by formation of an intermediate substance. Thus, in the action on 1:1 complexes of aqueous alcoholic solutions of pyridine, ethanolamine, ammonia (at room temperature), NaOH, Na_2CO_3, $NaHCO_3$ and CH_3COONa (with heating), the complexes at first go into solution to the accompaniment of an increase in color intensity, and later (at speeds varying for different reactants) the 1:2 complexes are formed. Transformation of the 1:1 complexes into 1:2 complexes also takes place on prolonged boiling with dilute alcohol in the absence of the above-noted reagents, although extremely slowly.



This transformation of the complexes does not take place in presence of acids (HCl, CH_3COOH). Acids act upon the 1:1 and 1:2 complexes with decomposition into the original azo compounds; the 1:1 complexes break down more slowly.

Reaction with heating of the 1:1 complexes of copper and o-hydroxy- and o-amino-o'-alkoxyazo compounds with pyridine or ethanolamine, in presence or absence of alcohol, leads to dealkylation and formation of complexes of the corresponding o-hydroxy- and o-amino-o'-hydroxyazo compounds. Formation of similar complexes also occurs on reaction of the starting o-hydroxy- and o-amino-o'-alkoxyazo compounds with copper sulfate in presence of pyridine or ethanolamine with heating. It is interesting that the resultant copper complexes have a 1:1:1 composition, i.e. they contain 1 atom of copper, 1 molecule of azo compound and 1 molecule of the base, e.g. ethanolamine.

EXPERIMENTAL

The objects of investigation were the monoazo compounds, prepared from o-phenetidine, o-aminodiphenyl and o-amino-o'-methoxydiphenyl ethers as diazo components and β-naphthol, 1-phenyl-3-methyl-5-pyrazolone, β-naphthylamine and 1-phenyl-3-methyl-5-aminopyrazole, as azo components.

o-Phenetidine was prepared by the usual method, starting from o-nitrophenolate. The o-aminodiphenyl [3] and o-amino-o'-methoxydiphenyl ethers were prepared by reducing the corresponding nitroethers; the latter were prepared by reacting o-nitrochlorobenzene with phenol [4] and correspondingly with guaiacol in alcoholic caustic soda solution. The azo compound was prepared by the usual method. The reaction conditions with the copper salts were similar to those described previously [1].

Copper salt of o-ethoxybenzenazo-β-naphthol (1:1 composition). Yellowish-brown rectangular plates (under microscope), did not melt upon being heated to 360°.

Found %: Cu 16.08; Cl 8.75; N 7.09. M 382 (in camphor). $C_{18}H_{15}O_2N_2ClCu$. Calculated %: Cu 16.29; Cl 9.09; N 7.18. M 390.3.

The action of concentrated sulfuric acid on the product, followed by dilution with water and recrystallization of the separated precipitate from ethyl alcohol, yielded a compound with m.p. 137.5-138°, which gave no depression with the initial dyestuff.

When the complex reacted with ammonia solution in dilute alcohol with heating (slowly at room temperature) or with pyridine at room temperature, 1 molecule of cupric chloride is lost per 2 molecules of the initial complex and a complex forms with a composition of 1:2, m.p. 244-245°, reddish-brown needles (under microscope).

Found %: Cu 8.05; Cl 8.53 (in solution); precipitate 83.1. For conversion $2C_{18}H_{15}O_2N_2ClCu \rightarrow (C_{18}H_{15}O_2N_2)_2Cu + CuCl_2$ Calculated %: Cu 8.15; Cl 9.09; of complex with composition 1:2, 82.72.

For substance with m.p. 244-245° Found %: Cu 9.76; azo compound 90.42. M 622. $(C_{18}H_{15}O_2N_2)_2Cu$. Calculated %: Cu 9.85; azo compound 90.46. M 645.6.

Copper salt of 1-phenyl-3-methyl-4-(o-ethoxybenzenazo)-5-pyrazolone. (1:1 composition). Long yellow needles (under microscope); m.p. 207-208° (with decomp.).

Found %: Cu 14.94; Cl 8.19; N 13.66. $C_{18}H_{17}O_2N_4ClCu$. Calculated %: Cu 15.13; Cl 8.44; N 13.33.

Copper salt of o-ethoxybenzenazo-β-naphthylamine (1:1 composition). It was prepared by reaction of initial azo compound with cupric chloride in alcoholic solution at room temperature; the precipitate that came down was immediately filtered off and washed with ethyl alcohol (without heating). Dark red, fine, long needles (under microscope); m.p. 177-179° (with decomp.).

Found %: Cu 16.10; N 10.91. $C_{18}H_{16}ON_3ClCu$. Calculated %: Cu 16.34; N 10.80.

1-Phenyl-3-methyl-4-(o-ethoxybenzenazo)-5-aminopyrazole. Orange-yellow prisms; m.p. 89.5-91° (from alcohol).

Found %: N 22.05. $C_{18}H_{19}ON_5$. Calculated %: N 21.80.

Copper salt (1:1 composition) was in the form of long yellow needles (under microscope); m.p. 186-187°.

Found %: Cu 14.96; N 16.82. $C_{18}H_{18}ON_5ClCu$. Calculated %: Cu 15.17; N 16.70.

The reactions of the last three copper salts of the ethoxyazo compounds (composition 1:1) with concentrated sulfuric acid, with aqueous-alcoholic ammonia and pyridine solution were analogous to those characteristic for the copper salt of o-ethoxybenzenazo-β-naphthol (1:1 composition) with the same reagents.

Copper salt of o-phenoxybenzenazo-β-naphthol (1:2 composition). When alcoholic solutions of o-phenoxybenzenazo-β-naphthol and cupric chloride were combined, the solution darkened and after some time had elapsed, a dark crystalline precipitate with a greenish luster separated out: microscopic brown, tetragonal prisms, m.p. 209°.

Found %: Cu 8.38; azo compound 91.96. $(C_{22}H_{15}O_2N_2)_2Cu$. Calculated%: Cu 8.57; azo compound 91.69.

The complex (1:1 composition) did not form when the above reagents were reacted in dilute solutions in the cold or with heating.

Reaction of coppers salts with other o-hydroxy-o'-phenoxyazo compounds. When alcoholic solutions of cupric chloride and 1-phenyl-3-methyl-4-(o-phenoxybenzenazo)-5-pyrazolone and also of p-phenoxybenzenazo-β-naphthylamine were combined complexes (1:1 composition) did not form. In this case, complexes (1:2 composition) formed which were identical to those prepared by the reaction of the same compounds with copper tetrammine sulfate in aqueous alcohol solution upon boiling the reagents for 1 hour.

Copper salt of 1-phenyl-3-methyl-4-(o-phenoxybenzenazo)-5-pyrazolone (1:2 composition). Brown, tetragonal, flat prisms (under microscope) with violet luster; m.p. 213.5-215°.

Found %: Cu 7.82; azo compound 92.07. $(C_{22}H_{17}O_2N_4)_2Cu$. Calculated %: Cu 7.93; azo compound 92.31.

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Copper salt of o-phenoxybenzenazo-β-naphthylamine (1:2 composition). Brown, tetragonal flakelets (under microscope) with green luster; m.p. 140-145° (depends considerably on rate of heating); at 170° the compound decomposed.

Found %: Cu 8.36; azo compound 91.52. $(C_{22}H_{16}ON_3)_2Cu$. Calculated %: Cu 8.59; azo compound 91.67.

Azo compound prepared from o-amino-o'-methoxydiphenyl ether and β-naphthol. Claret-colored needles with greenish luster; m.p. 167.5 – 169° (from ethyl alcohol).

Found %: N 7.61. $C_{23}H_{18}O_3N_2$. Calculated %: N 7.57.

Copper salt of dye prepared from o-amino-o'-methoxydiphenyl ether and β-naphthol (1:2 composition). It was prepared under the same conditions as described above; when the reagents reacted, the solution darkened appreciably. Brown prisms (under microscope); m.p. 210° (with decomp.).

Found %: N 6.73 $(C_{23}H_{17}O_3N_2)_2Cu$. Calculated %: N 6.99.

Complex (1:1 composition) did not form.

Reaction of copper salts of o-methoxy- and o-ethoxybenzenazo-β-naphthol (1:1 composition) with bases. A mixture of the complex, ethyl alcohol and the base (NH_4OH, NaOH, Na_2CO_3 and others) with a small amount of water was boiled with reflux condenser until the complete disappearance of the characteristic crystals of the complex (1:1 composition); the course of the reaction was regulated by microscopic examination of samples of the reaction mixture. After the reaction was complete, water was added to the reaction mixture, the precipitate was filtered off and identified by its melting point with the corresponding complex (1:2 composition). It was observed that the rate of conversion of complexes (1:1) into complexes (1:2) was affected by the enumerated reagents in the following order.

$NH_4OH > NaOH > Na_2CO_3 > NaHCO_3 > CH_3COONa > H_2O$.

The complexes were reacted with organic bases at room temperature or with heating: the complex dissolved in pyridine (or in ethanolamine) or alcohol was added to its pyridine solution. After the reaction was complete (5 minutes at room temperature or 4 hours with heating on a boiling water bath), water was added to the reaction mixture, the precipitate that formed was filtered off, washed with water and ethyl alcohol and identified.

The compounds that were separated after reaction of the complexes (1:1) with pyridine (or with ethanolamine) had gone for a short period, were identical to the complexes (1:2), prepared by reacting the corresponding azo compounds with copper tetrammine sulfate.

The compounds that were separated after the complexes (1:1) had reacted with pyridine (or with ethanolamine) with heating for a considerable length of time, were identical to each other and proved to be the copper complex of o-hydroxybenzenazo-β-naphthol; upon cleavage of the prepared complexes with concentrated sulfuric acid, an azo compound m.p. 193-194.5° separated out; a mixed sample of it with o-hydroxybenzenazo-β-naphthol gave no melting point depression.

When o-methoxybenzenazo-β-naphthol reacted with copper sulfate in a monoethanolamine medium, upon heating and subsequent cooling of the solution without addition of water, reddish-brown needles (under microscope) separated out which were the copper complex of o-hydroxybenzenazo-β-naphthol and monethanolamine.

Found %: N 10.98. $(C_{16}H_{10}O_2N_2)(C_2H_7ON)Cu$. Calculated %: N 10.86.

SUMMARY

1. A study was made of the interaction of copper salts with some o-hydroxy-o-amino-o'-ethoxy- and -o'-aroxyazo compounds. Copper complexes of azo compounds were prepared from o-phenetidine, o-aminodiphenyl and o-amino-o'-methoxydiphenyl ethers, as diazo components, and β-naphthol, 1-phenyl-3-methyl-5-pyrazolone, β-naphthylamine and 1-phenyl-3-methyl-5-aminopyrazole as azo components.

2. It was shown that 1:1 complexes of o-hydroxy-o'-alkoxyazo compounds can exist and that o-hydroxy-o'-aroxyazo compounds are incapable of forming complexes of this type.

3. Some properties of 1:1 copper complexes of o-hydroxy-o'-alkoxyazo compounds were studied with reference to a numberof representatives of the class.

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SOME SALTS OF IMIDOSULFAMIDE

L. M. Volshtein, N. N. Piserzhevskaya and M. M. Slutskaya

Up to recent times the existence of free imidosulfamide $NH_2SO_2NHSO_2NH_2$ had been regarded in the literature [1] as open to doubt. Data for the silver and ammonium salts have been published [1], but they are not very reliable. Thanks to the researches of Kirsanov [2], the existence of imodosulfamide has been conclusively established, and this substance is now easily accessible. Kirsanov revealed the strongly acidic properties of imidosulfamide and obtained salts of this acid with the cations: Na^+, NH_4^+, Ag^+, Ba^{++}, $C_6H_5NH_3^+$ and $C_5H_5NH^+$. The author did not study the physico-chemical properties of aqueous solutions of the synthesized salts. On the basis of the unusual behavior of a solution of the silver salt toward caustic alkalies, it was suggested (see below) that coordination bonds are present between the silver atoms and the amido groups of the imidosulfamide ion.

We have now continued the study of the character of the salts prepared by Kirsanov, and have also synthesized and investigated new salts of imidosulfamide. In the present communication we present new data for salts of Ba^{++} and Ag^+, and also describe the synthesis of the copper salt.

EXPERIMENTAL

Preparation of the salts. The barium salt was prepared by the Kirsanov [2] reaction of HIm* with $BaCO_3$. We prepared $BaIm_2$ by reacting sulfamide with $Ba(OH)_2$. A similar method was suggested by Kirsanov for the preparation of NaIm. 0.1 mole of sulfamide was added to a solution of $Ba(OH)_2$ in water, from which CO_2 had been eliminated (before addition, the solution was heated to the boiling point and then removed from the flame). The $Ba(OH)_2$ content in the solution was slightly (2%) less than 0.025 mole. The mixture strongly frothed. After 10 minutes of vigorous boiling, the solution was filtered while hot, the filtrate was evaporated down almost to dryness in vacuum at 40-50°. The oily mass which slowly crystallized was purified by being boiled with alcohol for a half hour, then was sucked off, washed with hot alcohol and dried to constant weight at 110°. We isolated about 10 g of salt.

Found %: Ba 27.99, 28.30; N 16.96, 17.00. $BaN_6H_8O_8S_4$. Calculated %: Ba 28.28; N 17.29.

The salt was white, readily soluble in water, and very difficulty soluble in alcohol. The reaction for the salt's preparation:

$$Ba(OH)_2 + 4NH_2SO_2NH_2 \rightarrow Ba[N(SO_2NH_2)_2]_2 + 2NH_3 + 2H_2O.$$

The silver salt was prepared by addition of $AgNO_3$ to concentrated $BaIm_2$ solution. A white finely crystalline precipitate immediately came down. The precipitate was set aside for a day, after which it was separated, washed with cold water and set aside in the dark in order to prepare the air-dried compound. Since the composition of the silver salt which crystallized in the form of the dihydrate was studied in detail by Kirsanov (prepared from $AgNO_3$ and NH_4Im), we limit ourselves to the statement that the composition of the salt $AgN(SO_2NH_2)_2 \cdot 2H_2O$ was corroborated by our analyses. Moreover, we prepared the anhydrous salt (by drying in vacuum at 40-50°), which we analyzed. Found: 38.34 and 38.45% Ag. Calculated: for the anhydrous salt ; 38.25% Ag.

We prepared the copper salt from $BaIm_2$ and $CuSO_4$, taken in molar ratio of 1:1. A weighed portion of the analyzed $BaIm_2$ was dissolved in a small volume of water, and the calculated volume of titrated $CuSO_4$ solution

* HIm represents free imidosulfamide. The anion of the acid $(NH_2SO_2)_2N$ is represented below by $\overline{Im}$.

was added to the above solution through a buret. The $BaSO_4$ precipitate was filtered off, and the filtrate was evaporated to low bulk in vacuum at 30-40°. The copper salt of imidosulfamide proved to be readily soluble in water. Evaporation was stopped when a considerable portion of the salt crystallized out. The blue crystals were separated from the mother liquor and dried to constant weight at 90°. After multiple determinations of the copper had been performed, we were convinced of the homogeneity of the prepared crystals and by repetition of the experiments we established the reproducibility of their composition.

Found %: Cu 14.69, 17.74; N 19.20, 19.45; S 29.74, 29.80. $CuN_6H_8O_8S_4 \cdot H_2O$. Calculated %: Cu 14.79; N 19.55; S 29.83. $CuN_6H_8O_8S_4$. Calculated %: Cu 15.43; N 20.41; S 31.13.

It was evident that the salt which was dried to constant weight at 90° was the monohydrate. The water of crystallization molecule was held very firmly. Drying of the salt at 120-140° did not cause dehydration; partial dehydration occurred in vacuum at 100°. The melting point of the salt was 149°. At first, we attempted to separate $CuIm_2$ from the concentrated aqueous solution by addition of alcohol. However, this method was not successful. It was observed that even when the $CuIm_2$ crystals were shaken with alcohol, a considerable change in the salt's composition took place.

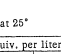
Electroconductivity of aqueous solutions of the salts. We measured (in a thermostat at 25°) the electroconductivity of $BaIm_2$ and $CuIm_2$ at concentrations of from 0.001 to 0.1 mole. For the slightly soluble AgIm, measurements were only in dilute solutions. All the measurements were repeated with the salt preparations prepared in different experiments, and the electroconductivity values proved reproducible within a range of 2%. The data obtained are given in the table.

TABLE

Equivalent Electroconductivity ($ohm^{-1}cm^2/g$-equiv.) of Imidosulfamide Salts at 25°

Salt	Concentration (in g-equiv. per liter)					
	0.001	0.002	0.01	0.02	0.04	0.2
$BaIm_2$	–	112	89	80	65	43
$CuIm_2$	–	108	86	76	–	44
AgIm	130	113	–	–	–	–

The molecular electroconductivity values for 0.002 N $BaIm_2$ and $CuIm_2$ solutions (224 and 216 $ohm^{-1}cm^2/$ mole) correspond to that of triple-ion electrolytes, which these salts should be. The molecular electroconductivity of AgIm solutions corresponded, as it should have, to that of a double-ion electrolyte. Therefore, the imidosulfamide salts are "simple" salts which do not exhibit stable coordinate bonds of metal atoms (Me) with the amido groups of the anion, the presence of which would considerably decrease the electroconductivity. It was especially important to establish this for AgIm, since the literature hypothesizes that structure of AgIm is cyclic. It is stated in Audrieth's [1] review article that: "Silver probably is bound to nitrogen, since treatment of AgIm with alkalis does not yield silver oxides". A similar hypothesis on the same basis was stated by Kirsanov [2]. However, we showed that AgIm gave all the characteristic reactions for Ag^+ ions in solution, and its peculiar reaction with alkali is explained by the interesting conversion which takes place, under these circumstances, of AgIm into the very difficulty soluble silver salt of sulfamide (see below).

We should remark that it could be expected beforehand that stable coordinate bonds would be absent in imidosulfamide salts since the formation of six-membered cycles Me  must be considered improbable. The formation of cyclic compounds with diamines is not characteristic of Ag^+. Such compounds are known to exist in the case of Cu^{++}. However, the tendency of the amido groups to coordination is decreased by immediate proximity to such groups as $-SO_2OH$ (in sulfamic acid) or $-SO_2NH-$. It is known [3] that copper sulfate is a "simple" salt and this also can be said of the salt $CuIm_2$ which we prepared.

Nevertheless, in concentrated solutions of $CuIm_2$ and $BaIm_2$, the appearance of unstable coordinate bonds is possible for Me with the amidogroups of the anion. Evidently, this is tied up with the factually observed, considerable decrease in the equivalent electroconductivity (λv) of the salts $CuIm_2$ and $BaIm_2$ in relatively concentrated

solutions. Thus, in 0.2 N solutions (see table) of these salts, λ_5 is less than 40% of λ_{500}, whereas for the majority of salts of the type $\overset{++}{Me}\bar{X}_2$, λ_5 is greater than 70% of λ_{500}.

The data of the table permit the approximate evaluation of the mobility of anion $\overline{Im}$. On the basis of the literature data, we see that λ_{500} for salts of the type $\overset{+}{Me}\bar{X}$ amounts to $\sim$ 0.97 of λ_∞, and for salts of type $\overset{++}{Me}\bar{X}_2$ $\sim$ 0.93 of λ_∞. We find that the magnitudes of λ_∞ for AgIm, $BaIm_2$ and $CuIm_2$ are approximately equal, being respectively 117, 120, 116 $ohm^{-1}cm^2$. Deducting from λ_∞ the mobility of the corresponding cations, we find the mobility values for the anion $\overline{Im}$ (at 25°) to be 55, 56 and 60 (on the average 57 $ohm^{-1}cm^2/g$-equiv.).

Conversion of AgIm into the silver salt of sulfamide. We have already noted that addition of alkalis to the AgIm solution did not cause Ag_2O to precipitate; a white, faintly cream-colored gelatinous precipitate formed, very difficulty soluble in cold and hot water and readily soluble in dilute HNO_3. Our experiments showed that the precipitate is the long known [1] silver salt of sulfamide. Found : 69.84, 69.42% Ag. Calculated for $Ag_2(NH)_2SO_2$: 69.63% Ag. A separate experiments showed that addition of NaOH to a solution of $AgNO_3$ containing an excess of sulfamide (as for the addition of NaOH to AgIm solution) did not cause Ag_2O to precipitate but it caused a precipitate of $Ag_2(NH)_2SO_2$ to come down. These facts lead us to conclude that the reason for the conversion of AgIm to $Ag_2(NH)_2SO_2$ must be the formation of a small quantity of sulfamide upon solution of the imidosulfamide salts in water. According to the data of Kirsanov [2], corroborated by us, the anion $\overline{Im}$ is stable in aqueous solution. However $\overline{Im}$ is subject in slight degree to conversion into sulfamide and sulfamate-ion:

$$NH_2SO_2NSO_2NH_2^- + H_2O \rightarrow NH_2SO_2NH_2 + OSO_2NH_2^- . \qquad (2)$$

Let us note that the neutral sulfamide solution does not yield a precipitate with Ag^+, and in the absence of alkali, AgIm does not convert to $Ag_2(NH)_2SO_2$. We supposed that upon addition of alkali to AgIm, the reaction would proceed according to the equation:

$$2AgN(SO_2NH_2)_2 + 2NaOH \rightarrow Ag_2(NH)_2SO_2 + NaOSO_2NH_2 + NaN(SO_2NH_2)_2 + H_2O. \qquad (3)$$

If this belief is correct, then after separation of $Ag_2(NH)_2SO_2$, we should find in the filtrate 50% of the initial quantity of the $\overline{Im}$ anions. We ran two parallel experiments and in each one we took 1 millimole of solid $AgIm \cdot 2H_2O$, added a millimole of NaOH(in the form of 0.1 molar solution), a drop of phenolphthalein and shook the mixture for 1 hour. We then separated off the precipitate of $Ag_2(NH)_2SO_2$ and added the wash waters to the filtrate. The alkali entered almost completely into the reaction (Equation 3), the filtrate was decolorized by several drops of 0.1 molar $AgNO_3$ solution. After this, a small excess of $AgNO_3$ solution was added to the filtrate. Immediately, a precipitate of AgIm started to come down. After 24 hours had elapsed, we separated the precipitate, washed it, and determined (by solution in HNO_3 and titration of the Ag with thiocyanate) the quantity of collected AgIm. We obtained 0.143 and 0.138 g of AgIm which amounts to 45 and 43.6% of the initial weight (0.318 g) of AgIm (to be sure, a small portion of the AgIm remained in filtrate and in the wash water as was to be expected). It is apparent, that the reaction in reality goes according to Equation (3).

Let us note, that $CuIm_2$, in contrast to AgIm, upon addition of alkali gave a precipitate $Cu(OH)_2$, i.e. no conversion takes place of $CuIm_2$ into the sulfamide salt. The experiment proved that the presence of an excess of sulfamide did not hinder the precipitation of the Cu^{++} ions with alkali. The literature, [1,2] notes the similarity between imidosulfamide and biuret. The latter, as is known, forms a complex anion with Cu^{++} in alkaline medium. However, HIm forms only a simple salt with Cu^{++}, completely decomposed by alkali.

SUMMARY

1. The copper salt of imidosulfamide $Cu[N(SO_2NH_2)_2]_2 \cdot H_2O$ is synthesized and described.

The preparation of the barium salt of imidosulfamide from sulfamide and barium hydrate is described.

2. A study is made of the electrical conductivity of aqueous solutions of the barium, silver and copper salts of imidosulfamide. It is shown that the salts are normal electrolytes and not inner-complex compounds.

3. It is shown that the silver salt of imidosulfamide is transformed into a salt of sulfamide under the action of caustic alkali.

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* T.p. = C.B. Translation pagination.

REACTIONS OF METALLIC OXIDES WITH ALCOHOLS

III. REACTIONS OF MANGANESE OXIDES WITH ISOPROPYL AND OTHER ALCOHOLS

V. A. Komarov, N. P. Timofeeva and T. M. Moroshkina

The reaction of oxides of manganese with alcohols is of interest in that manganese forms several oxides with different degrees of oxidation, so that we can expect changes in the composition of the oxides under the influence of alcohols and their decomposition products. The products of breakdown of alcohols in presence of manganous oxide has been studied by Sabatier and coworkers [1] and later by Taylor [2]. These authors found that on passing vapors of alcohols over heated manganous oxide at 320-425°, dehydrogenation takes place with formation of aldehyde (or ketone) and hydrogen, the process being complicated at higher temperatures by the following reactions: decomposition or condensation of the aldehyde with formation of carbon monoxide and disproportionation of the carbon monoxide to carbon dioxide and carbon. The action of manganous oxide in breakdown of alcohols is extremely similar to that of metallic copper but considerably weaker. Later work has also been published on the decomposition of alcohols over manganous oxide [3] which is consistent with the earlier work. As far as we are aware, the catalytic decomposition of alcohols in presence of other oxides of manganese and metallic manganese has not previously been studied; the same is true of the possible transformations of the solid phases concerned when heated in presence of alcohol vapors and their breakdown products. The establishment of such data was the objective of the present investigation within the framework of our investigations of interaction of metallic oxides with alcohols. The literature contains some data for reaction of metallic oxides with alcohols. Sabatier, for example, observed complete or partial reduction of some metallic oxides when used as catalysts of decomposition of alcohols [1]. Taylor and Williamson [2] showed that under the conditions of decomposition of ethyl alcohol over WO_3, the latter is gradually reduced to W_2O_5, the change being accompanied by a change in the selectivity of the catalyst. The concepts of the mechanism of contact phenomena, enunciated with penetrating genius by Mendeleev [5], account for the reciprocal effects of catalyst and reacting molecules.

Characteristics of the manganese preparations used. In the present investigation the catalysts used in decomposition of alcohols were electrolytically prepared metallic manganese and oxides of manganese, of which manganous oxide was obtained by calcination of manganese oxalate in a hydrogen stream and the remaining oxides by calcination of chemically pure manganese nitrate at appropriate temperatures [6]. The composition of the oxide preparations was established by chemical analysis, and their structure by x-ray examination. Due to the lack of an existing method of phase analysis of the system manganese - oxygen, our manganese preparations were analyzed for total manganese by titration in the divalent form in an alkaline medium [7] and by determination of manganese dioxide by the ferrous sulfate method [8]. The chemical and x-ray characteristics of the starting preparations are set forth in Table 1.

The data of Table 1 show that the preparation obtained by calcination of β-MnO_2 is a mixture of two manganese oxides with different structures and valences; the remaining oxides, and the metallic manganese, were homogeneous substances; the composition of some of them nevertheless deviated from the stoichiometric composition.

Experimental procedure and analytical methods. Experiments were conducted in an apparatus of the usual type, comprising a quartz tube, containing catalyst, placed in a tubular electric block furnace, a buret for addition of alcohol, a condenser, a receiver for condensate, and a cylindrical gasholder. The temperature was measured by a thermocouple in a quartz pocket; the junction of the couple was in the middle of the catalyst bed. Prior to the experiments at a specific temperature over each manganese preparation, the temperature of commence-

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ment of breakdown of the alcohol was determined by the previously described method [9]. After this determination, experiments were carried out at two temperatures, one of which was 20-25° and the other 40-45° higher than the temperature of commencement of reaction. The gas formed by decomposition of the alcohol was analyzed in a VTI apparatus for its content of CO_2, C_nH_{2n}, O_2, CO and H_2, and the condensate was examined by the hydroxylamine method for its content of carbonyl compounds. The activity of the preparations was evaluated on the basis of the volume of gas evolved, converted to the same volume, weight and surface of catalyst. The selectivity of the preparations was characterized by the value of the ratio of moles hydrogen to unsaturates, while the degree of deviation of the reactions from the normal route was characterized by the value of the ratio of moles hydrogen to carbonyl compounds. Calculation of the activity per unit of catalyst surface (of manganese preparation after its employment as catalyst of decomposition of alcohols) was facilitated by construction of isotherms of nitrogen adsorption at the temperature of liquid air [10], on the basis of which the specific surface was calculated by the B-E-T equation. The following values were obtained: metallic manganese 13.7, manganous oxide 20.0, Mn_2O_3 and Mn_3O_4 13.8, manganese dioxide 19.4 m^2/g.

TABLE 1

Chemical formula of preparation	Results of chemical analysis			Phase composition from x-ray data
	Total Mn (in %)	MnO_2 (in %)	Formula	
Mn (metallic)	100	–	Mn	β-Mn
MnO	76.9	–	$MnO_{1.03}$	Structure of NaCl type
Mn_2O_3	65.0	53.0	$MnO_{1.85}$	Mixture of hausmannite with one of the forms of braunite
MnO_2	57.0	85.5	$MnO_{2.58}$	Structure of the rutile type β-MnO_2

Results obtained in decomposition of alcohols on manganese preparations and from determination of the composition of the latter. Figs. 1 to 4 contain gas formation curves from which are found the temperatures of start of decomposition of isopropyl alcohol on metallic manganese and its oxides. It follows from Figs. 2 and 4 that prolonged employment of the preparations as catalysts leads to a rise in the temperature of commencement of reaction by 30-40°. Results of experiments on reaction of isopropyl alcohol with metallic manganese and its oxides are set forth in Table 2, and the results of examination of the manganese preparations before and after their use are shown in Table 3.

TABLE 2

Preparation	Temperature of experiment	Activity (in milliliters gas per 1 g alcohol passed) expressed per 1 ml	Activity expressed per 1 m^2	H_2/C_3H_6O	H_2/C_3H_6	Percent decomposed alcohol	Total of accounted products	E_A (kcal/mol)
Mn.	400°	1.6	0.066	1.0	14.2	10.7	91	21.8
	430	3.2	0.126	1.1	16.2	19.2	93	
MnO.	400	4.5	0.277	1.3	45.2	28.1	84	15.1
	440	8.5	0.515	1.8	29.0	31.9	78	
Mn_2O_3. . . .	420	2.96	0.160	1.0	30.4	20.0	101	15.0
	450	4.95	0.266	1.1	30.0	28.1	97	
MnO_2	350	3.38	0.105	1.1	21.5	19.1	94.5	12.2
	400	7.7	0.230	1.5	15.7	32.0	97.7	

Note. The data in this and the following tables are mean results of several experiments.

It follows from the data of Table 3 that the character of the decomposition of isopropyl alcohol over metallic manganese differs somewhat from that over its oxides. Decomposition over the metal starts at a higher temperature and requires a considerably higher activation energy. Both manganese and its oxides have relatively low activity, predominantly as dehydrogenation catalysts; however, over metallic manganese the dehydration reaction is more intensive than over the oxides. It is interesting to note that the effect of temperature on the course of the process over manganese is not the same as over the oxides: with rising temperature the dehydrating properties of metallic manganese are slightly enhanced but the dehydrating properties of the oxides are slightly diminished.

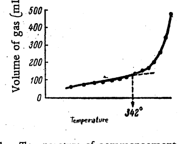

Fig. 1. Temperature of commencement of decomposition of isopropyl alcohol over metallic manganese.

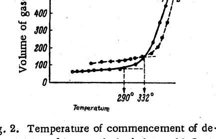

Fig. 2. Temperature of commencement of decomposition of isopropyl alcohol over MnO. 1) Before use, 2) after use.

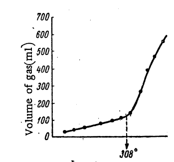

Fig. 3. Temperature of commencement of decomposition of isopropyl alcohol on Mn_2O_3.

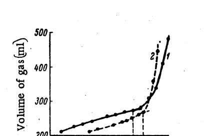

Fig. 4. Temperature of commencement of decomposition of isopropyl alcohol over MnO_2. 1) Before use, 2) after use.

TABLE 3

Preparation	Temperature	Result of chemical analysis: % total Mn, Before expt.	% total Mn, After expt.	% MnO_2, Before expt.	% MnO_2, After expt.	Formula, Before expt.	Formula, After expt.	X-ray data: Before expt.	X-ray data: After expt.
Mn	400°	100	100	—	—	Mn	Mn	Lattice β-Mn	Lattice β-Mn
Mn	430	100	98.5	0	1.5	$MnO_{0.00}$	$MnO_{0.05}$		
MnO . . .	400	76.9	74.7	0	1.15	$MnO_{1.03}$	$MnO_{1.16}$	Lattice MnO	Lattice MnO
MnO . . .	440	74.7	72.4	1.15	1.20	$MnO_{1.16}$	$MnO_{1.20}$		
Mn_2O_3 . .	420	65.0	—	53.0	—	$MnO_{1.85}$	—	Mixture of hausmannite and braunite	Lattice MnO
Mn_2O_3 . .	450	—	76.5	—	4.4	$MnO_{1.05}$	—		
MnO_2 . . .	350	57.0	73.9	85.3	3.8	$MnO_{2.3}$	$MnO_{1.2}$	β-MnO_2	Lattice MnO
MnO_2 . . .	400	73.9	71.0	3.8	2.1	$MnO_{1.2}$	$MnO_{1.4}$		

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From an inspection of the H_2/C_3H_6 and H_2/C_3H_6O ratios, we can conclude that in the series $MnO_2 - Mn_2O_3 - MnO$ the dehydrating ability falls slightly and that in all cases, except MnO at 440° and MnO_2 at 400°, deviations from the normal reaction course are insignificant. A noteworthy feature is the very large proportion of CO_2 in the gas obtained over MnO_2 and Mn_2O_3 at the start of reaction. This is associated with partial oxidation of the alcohol which commences at temperatures below the decomposition temperatures. Chemical and X-ray analysis of the manganese preparations established that during the process of reaction with isopropyl alcohol and its decomposition products, all the oxides of manganese acquire the structure of sodium chloride (characteristic of MnO) and they more or less approximate to the composition of MnO with an excess of oxygen over the stoichiometric formula. Metallic manganese retains its structure, evidently being covered at the surface with an extremely thin film of oxides of manganese. Similar results were obtained in an investigation of the reaction of ethyl alcohol with metallic manganese and its oxides. Below (Table 4) are presented the results of experiments on decomposition of some alcohols over β-MnO_2.

TABLE 4

Alcohol	Temperature of expts.	Activity (ml gas/g alcohol passed/ml oxide)	Ratio of moles H_2 to		E_A kcal/mol	T_{comm}	Chem. composition of preparations after experiments		
			carbonyl compounds	unsaturated compounds			Content in %		Formula
							of total Mn	MnO_2	
C_2H_5OH	400°	8.3	4.9	26.0	13.3	340	74	11	$MnO_{1.2}$
	440	14.5	6.0	17.0			72	4	$MnO_{1.3}$
C_3H_7OH	350	4.3	1.2	21.3	12.2	340	71.2	2.4	$MnO_{1.4}$
	400	8.9	1.6	15.7					
C_4H_9OH	400	5.6	2.5	13.0	15.0	360	73.8	4	$MnO_{1.22}$
	440	10.5	2.4	12.0					
$C_5H_{11}OH$	415	8.1	2.8	45.0	26.0	380	67.3	2.0	$MnO_{2.0}$
	450	12.8	4.7	29.0					

The data of Table 4 show that all the investigated alcohols mainly undergo dehydrogenation over β-MnO_2, and the β-MnO_2 is reduced during the process to $MnO_{1.2}$–$MnO_{1.4}$; the x-ray data show that it has the MnO structure. Table 4 also indicates that with rising molecular weight of the alcohol both the temperature of commencement of reaction and the activation energy increase, and the character of the decomposition changes slightly.

It is interesting to compare the interatomic distances of the manganese preparations (Mn – Mn and Mn – O) with the character of the decomposition and the temperature of its commencement. Data for these are presented in Table 5.

TABLE 5

Preparation	Temperature of experiment	% decomposition	H_2/C_3H_6	T_{comm}	Interatomic distances (in A)		
					Mn – Mn	Mn – O	O – O
Mn	400°	10.7	14.2	342°	3/2.36 5/2.53 2/2.60 14/2.67	–	–
MnO	400	28.1	45.2	290	12/3.125 6/4.42	6/2.21 8/3.83	12/3.125 6/4.42
Mn_2O_3	420	20	30.4	308	12/3.15 12/3.55	12/2.01	6/2.52
MnO_2	400	32	15.7	308	2/2.87 8/4.398	– 6/1.89 4/3.43	1/2.55 8/(2.67) 2/2.87 2/(3.64)

Note: In the last 3 columns the numerator denotes the number of neighbors, the denominator the corresponding interatomic distances.

The values in Table 5 lead us to the conclusion that both directions of decomposition of the alcohol proceed at metal atoms, the smallest Me – Me distance favoring in some degree the dehydration reaction. This conclusion conflicts, however, with the results of A. M. Rubinshtein [11] on decomposition of ethyl alcohol over a series of manganese oxide preparations and those of N.I. Egorova [12] on decomposition of ethyl alcohol over oxides of vanadium, columbium and titanium.

SUMMARY

1. In the reaction of manganese oxides with isopropyl alcohol, decomposition of the alcohol (with predominant formation of hydrogen and acetone) is accompanied by reduction of MnO_2 and Mn_2O_3 to MnO; the latter oxide has a certain excess of oxygen over the stoichiometric amount.

2. Under the same conditions, metallic manganese only undergoes very slight surface oxidation; the predominating direction of the reaction is dehydrogenation, but dehydration proceeds to a greater extent than on the oxides.

3. The activation energy of the decomposition of isopropyl alcohol over metallic manganese and the temperature of commencement of this reaction are considerably higher than the corresponding values for oxides of manganese.

4. The temperature of commencement of reaction of alcohols with β-MnO_2 rises with increasing molecular weight of the alcohol.

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SYNTHESIS OF HYDROCARBONS

LIII. ISOPRENE HYDROBROMIDE IN THE SYNTHESIS OF HYDROCARBONS WITH A QUATERNARY ATOM – TERT -ALKYLETHYLENES

R. Ya. Levina, V. R. Skvarchenko and T. M. Ushakova

One of the most convenient and most highly developed methods of synthesis of alkenes of various structures is the reaction between organomagnesium compounds and allyl halides and their homologs. Homologs of allyl chloride or bromide are easily obtained by the action of hydrogen chloride or bromide on hydrocarbons containing a conjugated system of double bonds.

Addition of hydrogen bromide to isoprene gives a mixture of isomeric bromides: 4-bromo-2-methylbutene-2 (primary bromide I) and 2-bromo-2-methylbutene-3 (tertiary bromide II) [1-3]. Consequently the reaction of isoprene hydrobromide with organomagnesium compounds ought to lead to two hydrocarbons (III and IV) of which one, obtained from the tertiary bromide (II) should possess a quaternary carbon atom (IV).

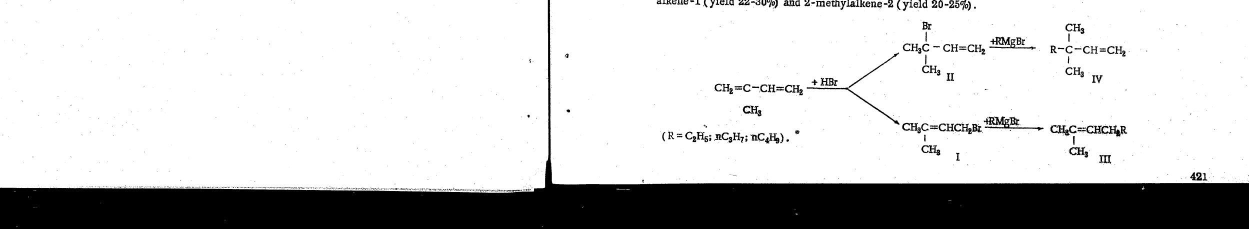
Claisen [2], and later one of us [4], showed that in the condensation of isoprene hydrobromide with phenyl- and cyclohexyl-magnesium bromide, conducted under the usual conditions, the primary hydrobromide (I) is mainly involved, and the corresponding hydrocarbons with a quaternary carbon atom were not isolated from the reaction products.

In one of our previous communications [5] the reaction between isoprene hydrobromide and methyl magnesium bromide was applied to the synthesis of 2-methylpentene-2, which is also formed from the primary hydrobromide.

In the present investigation we aimed at finding the conditions for possible application of the reaction between isoprene hydrobromide and organomagnesium compounds to the synthesis of α-ethylenic hydrocarbons with a quaternary carbon atom – tertiary alkylethylenes (IV) – which hitherto have been very inaccessible and synthesized mainly by pyrolysis of the acetates of pinacolinic alcohols [6].

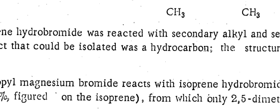
It was found that reaction at low temperature (–70°) improves the stability of the tertiary isoprene hydrobromide (II); under these conditions the latter does not undergo the allyl rearrangement to the primary bromide (I) (or only rearranges in part) and it enters into reaction with organomagnesium compounds to form a hydrocarbon with a quaternary carbon atom (yield 22-30%).

Thus, the reaction of isoprene hydrobromide (immediately after its preparation without distillation) with primary alkyl magnesium bromides, carried out with cooling to –70°, led to formation in each reaction of a mixture of two hydrocarbons in total yield of 55-59%; fractionation of the mixture in a column gave 3,3-dimethylalkene-1 (yield 22-30%) and 2-methylalkene-2 (yield 20-25%).



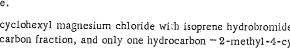
$(R = C_2H_5;\ nC_3H_7;\ nC_4H_9)$. *

In the reaction of isoprene hydrobromide with isobutyl magnesium bromide the total yield of alkenes was 30%; from this mixture two hydrocarbons were separated: 3,3,5-trimethylhexene-1 (6%) and 2,6-dimethylheptene-2 (9%):



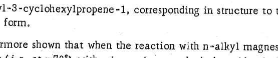
When isoprene hydrobromide was reacted with secondary alkyl and secondary cycloalkyl magnesium halides the only product that could be isolated was a hydrocarbon; the structure corresponded to primary isoprene hydrobromide.

Thus, isopropyl magnesium bromide reacts with isoprene hydrobromide to form a mixture of hydrocarbons (total yield 36%, figured on the isoprene), from which only 2,5-dimethylhexene-2 (23%) was isolated.



3,3,4-Trimethylpentene-1, corresponding in structure to tertiary isoprene hydrobromide, could not be isolated in the pure state.

Reaction of cyclohexyl magnesium chloride with isoprene hydrobromide at −70° led to a much lower yield (21%) of hydrocarbon fraction, and only one hydrocarbon – 2-methyl-4-cyclohexylbutene-2 (yield 12%) – could be isolated:



3,3-Dimethyl-3-cyclohexylpropene-1, corresponding in structure to tertiary isoprene hydrobromide, was not isolated in pure form.

It was furthermore shown that when the reaction with n-alkyl magnesium bromides was performed under the same conditions (i.e. at −70°) with primary isoprene hydrobromide (isolated in the pure form), only one hydrocarbon is formed, corresponding to this hydrobromide – 2-methylalkene-2.

Consequently, if the objective of the reaction is the synthesis of tertiary alkylethylenes, then the reaction with organomagnesium compounds should be carried out at −70°, using undistilled isoprene hydrobromide (immediately after its preparation).

EXPERIMENTAL

Isoprene hydrobromide was prepared by the addition of a stoichiometric quantity of dry hydrogen bromide upon cooling to −70°, to isoprene (previously distilled on a column, b.p. 33.5-34° at 760 mm, n_D^{20} 1.4220); the reaction mass was diluted with absolute ether (1:1) and immediately reacted with the alkylmagnesium bromide.

Reaction of isoprene hydrobromide with alkylmagnesium halides at −70°.

An ethereal solution of isoprene hydrobromide (prepared from 36 g, 0.5 mole isoprene), cooled to −70°, was added drop-wise with mechanical stirring, to the alkylmagnesium bromide (prepared from 24 g of magnesium, 1 mole of alkyl bromide in 300 ml of absolute ether), cooled to −70°. After addition of all of the hydrobromide, the reaction mixture was stirred for 2 hours at −70° and was left to stand overnight. The next day, stirring was continued for 4-5 hours at room temperature; the compound was decomposed with 10% acetic acid. The ethereal extract was washed until it gave a neutral reaction and dried with calcium chloride. The ether was driven off the residue was boiled (with reflux condenser) with sodium to remove traces of the unreacted hydrobromide, driven off from the high-boiling dimer of isoprene which had formed during the reaction and then distilled in a column over sodium.

When isoprene hydrobromide reacted with ethylmagnesium bromide under the described conditions, we obtained

27 g of hydrocarbon mixture (55% on the basis of isoprene) from which we isolated two hydrocarbons:

1) 3,3-Dimethylpentene-1 (14.6 g; 30% of theoretical).

B.p. 76.5-77° (755 mm), n_D^{20} 1.4000, d_4^{20} 0.6965, MR_D 34.17. C_6H_{14} ⌈̅. Calculated 34.06. The literature data give [7]: b.p. 76.9° (760 mm), n_D^{20} 1.3991, d_4^{20} 0.6961. The dibromide prepared from this hydrocarbon (1,2-dibromo-3,3-dimethylpentane) had the following constants:

B.p. 104-104.5 (20 mm), 96° (8 mm), n_D^{20} 1.5089, d_4^{20} 1.5570, MR_D 49.66. $C_7H_{14}Br_2$. Calculated 50.05.

2) 2-Methylhexene-2 (10 g, 20% of theoretical).

B.p. 94-94.5° (755 mm), n_D^{20} 1.4127, d_4^{20} 0.7100, MR_D 34.46. Literature data [8] give: b.p. 95.41° (760 mm), n_D^{20} 1.4103, d_4^{20} 0.7081.

3) Intermediate fraction (2g) b.p. 77-93.5° (755 mm), n_D^{20} 1.4053.

When isoprene hydrobromide was reacted with propylmagnesium bromide under the same conditions, we also obtained a mixture of two hydrocarbons (34.7 g, 59% of theoretical) from which we isolated:

1) 3,3-Dimethylhexene-1 (13.5 g, 22% of theoretical).

B.p. 103.5-104° (750 mm), n_D^{20} 1.4080, d_4^{20} 0.7127, MR_D 38.49. C_8H_{16} ⌈̅. Calculated 38.67. Literature data [9] give: b.p. 104° (760 mm), n_D^{20} 1.4070, d_4^{20} 0.7143.

2) 2-Methylheptene-2 (14.6 g, 25% of theoretical).

B.p. 121.5° (750 mm), n_D^{20} 1.4180, d_4^{20} 0.7205, MR_D 38.86. Literature data [8] give: b.p. 122.6° (760 mm), n_D^{20} 1.4172, d_4^{20} 0.7241.

3) Intermediate fraction (3.1 g) had b.p. 104.5-121.5° (750 mm), n_D^{20} 1.4140.

A low-boiling fraction was also separated (2.5 g), boiled up to 102.5°, n_D^{20} 1.3990, and was, evidently, a mixture of hexane and 3,3-dimethylhexene-1. Literature data for hexane [10] give: b.p. 68.3°, n_D^{20} 1.3752.

The reaction of isoprene hydrobromide with butylmagnesium bromide yielded a mixture of two hydrocarbons* (37 g, 58% of theoretical), which upon distillation, yielded:

1) 3,3-Dimethylheptene-1 (14.7 g, 23% of theoretical).

B.p. 128° (741 mm), n_D^{20} 1.4150, d_4^{20} 0.7295, MR_D 43.33. C_9H_{18} ⌈̅. Calculated 43.29. Literature data [9] give: b.p. 128.8° (760 mm), n_D^{20} 1.4145, d_4^{20} 0.7295.

The dibromide prepared from this hydrocarbon (1,2-dibromo-3,3-dimethylheptane), had the following constants:

B.p. 118° (10 mm), 112-112.7° (7 mm), n_D^{20} 1.5020, d_4^{20} 1.4382, MR_D 58.95. $C_9H_{18}Br_2$. Calculated 59.29.

2) 2-Methyloctene-2 (15.3 g, 24% of theoretical).

B.p. 144-145° (741 mm), n_D^{20} 1.4240, d_4^{20} 0.7383, MR_D 43.57. Literature data [9] give: b.p. 146.2° at 760 mm, n_D^{20} 1.4240, d_4^{20} 0.7385.

3) Intermediate fraction (5 g) had boiling range 128-144° (741 mm), n_D^{20} 1.4180.

When isoprene hydrobromide was reacted with isobutylmagnesium bromide, we obtained a mixture of hydrocarbons (19.3 g, 30% theoretical), from which we isolated:

1) 3,3,5-Trimethylhexene-1 (4 g, 6% of theoretical).

B.p. 121-121.5° (747 mm), n_D^{20} 1.4120, d_4^{20} 0.7271, MR_D 43.11. C_9H_{18} ⌈̅. Calculated 43.29. Literature data [9] give: b.p. 121.5° (760 mm), n_D^{20} 1.4139, d_4^{20} 0.7280.

2) 2,6-Dimethylheptene-2 (5.8 g, 9% of theoretical).

B.p. 138-139° (747 mm), n_D^{20} 1.4215, d_4^{20} 0.7322, MR_D 43.76. Literature data give: b.p. 138.9° (760 mm), n_D^{24} 1.4224, d_4^{20} 0.7336 [9]; b.p. 142-143°, n_D^{20} 1.4321, d_4^{20} 0.768 [12].

* Aside from the two alkenes cited, we separated a fraction 7.6 g, which boiled up to 128°, n_D^{20} 1.4080, which was, evidently, a mixture of octane and 3,3-dimethylheptene-1 (literature data for octane [11] give: b.p. 125.6° at 760 mm, n_D^{20} 1.3978).

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3) Intermediate fraction (3 g) boiled at 121.5-138° (747 mm); n_D^{20} 1.4237. Low-boiling fraction (6.5 g, boiled up to 120°, n_D^{20} 1.4011) contained, evidently, 2,5-dimethylhexane (literature data [13] give: b.p. 109.2° at 760 mm, n_D^{20} 1.3932) mixed with 3,3,5-trimethylhexene-1.

The reaction of isoprene hydrobromide with isopropylmagnesium bromide, under the above described conditions, yielded a hydrocarbon mixture (21 g, 36% theoretical) from which we isolated 2,5-dimethylhexene-2 (13.7 g, 23% of theoretical):

B.p. 111.5-112° (747 mm), n_D^{20} 1.4150, d_4^{20} 0.7186, MR_D 38.80. $C_8H_{16}\overline{|}$. Calculated 38.67. Literature data [14] give: b.p. 111.2-111.5° (747 mm), n_D^{20} 1.4120, d_4^{20} 0.7182.

Low-boiling fraction (6.3 g), boiling range 103-111.5° and n_D^{20} 1.4140 was a mixture of 3,3,4-trimethylpentene-1 and 2,5-dimethylhexene-2. Literature data for 3,3,4-trimethylpentene-1 [9] give: b.p. 105.4°, n_D^{20} 1.4140, d_4^{20} 0.7287. The fraction that boiled up to 103.5° was, evidently, a mixture of 3,3,4-trimethylpentene-1 and 2,3-dimethylbutane (literature data for 2,3-dimethylbutane [15] give: b.p. 58°, n_D^{20} 1.3751).

The reaction of isoprene hydrobromide with cyclohexylmagnesium chloride also yielded a hydrocarbon mixture (22.4 g, 21% theoretical), which upon fractionation, yielded 2-methyl-4-cyclohexylbutene-2 (9.6 g, 12% of theoretical):

B.p. 75° (11 mm), n_D^{20} 1.4635, d_4^{20} 0.8258, MR_D 50.79. $C_{11}H_{20}\overline{|}$. Calculated 50.33. Literature data [4] give: b.p. 101-102.5° (40 mm), n_D^{20} 1.4635, d_4^{20} 0.8283.

Besides this, we obtained a low-boiling fraction that boiled at 40-75° (11 mm), n_D^{20} 1.4505, which possibly contained a hydrocarbon with a quaternary carbon atom – 3,3-dimethyl-3-cyclohexylpropene-1.

Reaction of primary isoprene hydrobromide (4-bromo-2-methylbutene-2) with butylmagnesium bromide.

Isoprene hydrobromide was prepared by the usual method and was vacuum-distilled twice; the fraction was collected that boiled at 60-65° (63 mm) and was primary bromide (I) – 4-bromo-2-methylbutene-2.

Literature data give: b.p. 62-64° (67 mm) [2]; b.p. 82-83° (150 mm) [16]; b.p. 77-78.5° (135 mm) [17].

The reaction of the primary isoprene hydrobromide (33.4 g, 0.22 mole) with butylmagnesium bromide and the separation of the reaction products was performed under the same conditions as described above. From the obtained hydrocarbon fraction, fractionation yielded 2-methyloctene-2 (10.2 g, 36% on the basis of isoprene), b.p. 144.5-145.2° (745 mm), n_D^{20} 1.4252, d_4^{20} 0.7389.

From the low-boiling fraction, containing octane, 2-methyloctene-2, and possibly, 3,3-dimethylheptene-1, we could not completely isolate the latter by itself.

SUMMARY

1. The reaction of alkyl magnesium bromides with isoprene hydrobromide (immediately after its preparation, without distillation) was studied at low temperature (–70°); it was shown that this reaction can serve as a preparative method of synthesis of 2-methylalkene-2 and of alkenes with a quaternary carbon atom – 3,3-dimethylalkenes-1 (in total yield of 55-59%), which are readily fractionated by distillation.

2. Reaction of isoprene hydrobromide with alkyl magnesium bromides (RMgBr where R = C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9, C_6H_{11}) gave 3,3-dimethylpentene-1, 3,3-dimethylhexene-1, 3,3,5-trimethylpentene-1, 2-methylhexene-2, 2-methylheptene-2, 2,5-dimethylhexene-2 and 2-methyl-4-cyclohexylbutene-2.

3. A study was made of the reaction at –70° of butyl magnesium bromide with primary isoprene hydrobromide – 4-bromo-2-methylbutene-2 – prepared in the pure form; only one alkene was isolated from the products of this reaction – 2-methyloctene-2 (yield 36%).

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REACTION OF DIOXANE WITH ACETIC ACID AND ACETIC ANHYDRIDE

K. N. Kovalenko, N. A. Trifonov and D. S. Tissen

Dioxane is now extensively used as a solvent. Undoubted interest is therefore attached to elucidation of the character of its interaction with substances belonging to various classes of chemical compounds. This accounts for the large number of publications devoted to dioxane solutions [1,2]. It is quite natural that dioxane, through the medium of its oxygen atoms, should enter into chemical interaction with substances containing polar groups in which hydrogen is present [3]. In particular, we should expect dioxane to react with organic acids due to formation of a hydrogen bond. We confirmed this experimentally in an investigation of the system dioxane – acetic acid by measurements of viscosity, density, surface tension and refractive index at 25 and 40°. On the other hand in the system dioxane – acetic anhydride (whose molecule is lacking in a hydrogen atom linked to a polar group), which we also studied with reference to the same properties, chemical reaction does not take place.

EXPERIMENTAL

Dioxane, pure grade, was kept for a long period over anhydrous calcium chloride, distilled, dried with metallic sodium and fractionally distilled over sodium. We used a fraction with b.p. 101-101.3° at normal pressure; d_4^{25} 1.0265, n_D^{25} 1.4204

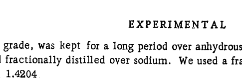
Acetic anhydride was kept over dehydrated sodium acetate and distilled over the latter at the ordinary pressure. The fraction collected for investigation had b.p. 138.8-139°, d_4^{25} 1.0737, n_D^{25} 1.3880.

Acetic acid was prepared from acetic anhydride, purified as above, by mixing with the calculated amount of water. d_4^{25} 1.0452, n_D^{25} 1.3710.

Viscosity was measured with the help of a capillary viscometer fitted with suitable devices for protecting the solutions against access of moisture; density was determined with a Regnault pycnometer, capacity approx. 5 ml; surface tension was measured by the method of lowest pressure of formation of bubbles; the constant of the capillary tip was 7.1. Refractive index was measured on a universal laboratory refractometer (Abbé type) with a thermostatic device enabling the required temperature to be maintained to an accuracy of $\pm$ 0.1°.

System dioxane – acetic acid. Results of measurements of viscosity (η), density (d), surface tension (σ) and refractive index (n_D) of the system are presented in Tables 1 and 2, where α and γ are the absolute temperature coefficients of viscosity and surface tension, $\Sigma V - V$ are the contractions in the system calculated by the Biron formula [4], and $n_{D\,add}^{25}$ are the values of refractive index at 25° calculated from the law of mixing with allowance for the additivity effect in the system when the composition is expressed in proportions by volume [5].

The viscosity and surface tension isotherms plotted in Fig. 1 point to the correctness of our assumption. On the viscosity isotherms there is a maximum lying close to the ordinate of the solution containing 33.3 mol.-% dioxane. This maximum testifies to the occurrence of chemical interaction between dioxane and acetic acid, leading to the formation of dissociated dioxane diacetate:



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Not less convincing are the surface tension isotherms whose form is characteristic of irrational systems[6-8].

TABLE 1

Viscosity and Surface Tension of the System Dioxane – Acetic Acid

CH_3COOH (mol-%)	η (in centipoises) 25°	40°	$\alpha = \frac{\eta_{t_1} - \eta_{t_2}}{t_2 - t_1}$	σ^{25}	σ^{40}	$\gamma = \frac{\sigma_{t_1} - \sigma_{t_2}}{t_2 - t_1}$
0	1.181	0.919	0.0174	33.65	31.53	0.141
20	1.187	0.920	0.0178	33.01	31.30	0.114
40	1.285	0.981	0.0202	32.52	30.75	0.118
60	1.333	1.013	0.0213	31.70	30.00	0.113
80	1.332	1.012	0.0213	29.34	27.64	0.113
100	1.193	0.921	0.0181	27.57	26.07	0.100

TABLE 2

Density and Refractive Index of the System Dioxane – Acetic Acid

CH_3COOH (mol-%)	CH_3COOH (vol.-%)	d_4^{25}	d_4^{40}	$\Sigma V - V$	n_D^{25}	n_D^{40}	$n_{D\,add}^{25}$	Deviation from additivity of the values Δn_D^{25} (V)
0	0	1.0265	1.0101	—	1.4204	1.4126	—	—
20	14.16	1.0348	1.0185	+0.50	1.4145	1.4072	1.4134	+0.0011
40	30.52	1.0411	1.0245	+0.71	1.4068	1.4000	1.4053	+0.0015
60	49.76	1.0434	1.0268	+0.53	1.3973	1.3908	1.3957	+0.0016
80	72.52	1.0442	1.0285	+0.27	1.3853	1.3790	1.3845	+0.0008
100	100	1.0453	1.0295	—	1.3710	1.3662	—	—

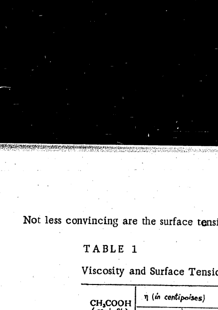

Fig. 1. System dioxane – acetic acid. Viscosity and surface tension and their temperature coefficients.

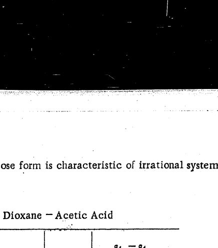

Fig. 2. Density and refractive index of the system dioxane – acetic acid.

Adsorption of acetic acid is masked on the surface tension isotherms by the chemical reaction in the system; on the curve of the temperature coefficient of the surface tension this phenomenon is reflected in the sharp drop of γ on addition of acetic acid to the dioxane ($\gamma_{CH_3COOH} = 0.100$, and $\gamma_{C_4H_8O_2} = 0.141$).

In Fig. 2 are plotted the density and refractive isotherms of the system dioxane – acetic acid, which likewise support our assumption; the composition is expressed in volume-percent [5,9]. The density isotherms reflect the marked contraction in the system; the refractive index isotherms point to a slight positive deviation from additivity. Both features are associated in the present case with reaction between the components.

System dioxane - acetic anhydride. Results of measurements of η, d, σ and n_D are presented in Tables 3 and 4.

TABLE 3

Viscosity and Surface Tension of the System Dioxane – Acetic Anhydride

$(CH_3CO)_2O$ (mol-%)	Viscosity (in centipoises) η^{25}	η^{40}	$\alpha = \frac{\eta_{t_1} - \eta_{t_2}}{t_2 - t_1}$	σ^{25}	σ^{40}	$\gamma = \frac{\sigma_{t_1} - \sigma_{t_2}}{t_2 - t_1}$
0	1.181	0.919	0.0174	33.65	31.53	0.141
20	1.027	0.826	0.0134	33.25	31.17	0.138
40	0.946	0.763	0.0123	32.87	30.89	0.133
60	0.891	0.728	0.0108	32.60	30.75	0.130
80	0.860	0.708	0.0101	32.44	30.47	0.130
100	0.842	0.693	0.0099	32.16	30.20	0.130

TABLE 4

Density and Refractive Index of the System Dioxane – Acetic Anhydride

$(CH_3CO)_2O$ (mol-%)	$(CH_3CO)_2O$ (vol.-%)	d_4^{25}	d_4^{40}	n_D^{25}	n_D^{40}	$n_{D\,add}^{25}$	Deviation from additivity of values of Δn_D (V)
0	0	1.0265	1.0101	1.4204	1.4126	—	—
20	21.68	1.0362	1.0205	1.4130	1.4057	1.4132	–0.0002
40	42.44	1.0465	1.0302	1.4064	1.3992	1.4066	–0.0002
60	62.40	1.0557	1.0394	1.3997	1.3925	1.4001	–0.0004
80	81.56	1.0653	1.0473	1.3940	1.3867	1.3941	–0.0001
100	100	1.0737	1.0557	1.3880	1.3820	—	—

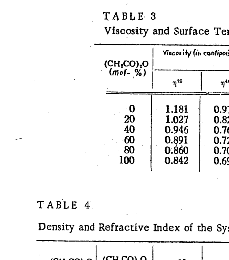

Fig. 3. System dioxane – acetic anhydride. Viscosity and surface tension and their temperature coefficients.

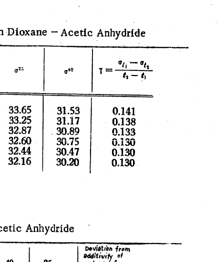

Fig. 4. Density and refractive index of the system dioxane – acetic anhydride.

We see from Figs. 3 and 4 that the isotherms of all the properties (except viscosity) that we studied are straight or nearly straight lines. The viscosity isotherms are convex to the axis of composition. Chemical interaction is clearly absent from the system dioxane – acetic anhydride. We may say that this system is almost normal in respect of reaction between the components. This fact confirms the correctness of our above suggestion about the character of the bond formed by interaction of dioxane with acetic acid.

SUMMARY

1. Systems dioxane – acetic acid and dioxane – acetic anhydride were studied by measurements of viscosity, density, surface tension and refractive index at 25 and 40°.

2. Chemical reaction is observed in the system dioxane – acetic acid, leading to formation of a compound which is considerably dissociated in solution.

3. The system dioxane – acetic anhydride is close to normal in respect of reaction between the components.

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INVESTIGATIONS ON CONJUGATED SYSTEMS

LX. REACTION OF DIVINYLETHYLACETYLENE WITH TERTIARY BUTYL CHLORIDE AND BROMIDE

A. A. Petrov and K. V. Leets

One of us (with Yu. I. Porfiryeva and E. A. Leporskaya) had previously shown that the simplest addends can be classified into two groups according to the order of addition to homologs of vinylacetylene. Hydrogen and hydrogen halides add on at the triple bond, halogens and hypohalites predominantly at the double bond [1-5]. In the case of vinylacetylene itself, all these addends add on exclusively or mainly at the triple bond [6].

These regularities in the reactivity of vinylacetylenic hydrocarbons may be correlated with the character of the displacement of electrons in the conjugated system under the influence of radicals, and also with steric factors. A larger number of facts must, however, be accumulated for establishment of the actual reasons for the regularities.

Special interest was merited by a study of reactions of vinylacetylenic hydrocarbons with halogen derivatives of hydrocarbons. The latter usually add on in the same direction as hydrogen halides [7], although the positively polarized portion is here not the hydrogen but the hydrocarbon radical. In the case of vinylacetylene this general law is observed. Tertiary butyl chloride and bromide in presence of zinc halides add on to vinylacetylene at the triple bond, the radical going to the first atom of the conjugated system and the halogen to the second [8]. α-Chloroethers add on to vinylacetylene likewise at the triple bond, mainly in the 1,2-position [9].

The results of experiments on reaction of vinylacetylene with tertiary butyl chloride and bromide in presence of the corresponding zinc halides also showed a different order of addition: the radical goes to the quaternary carbon atom of the conjugated system, and the halogen to the first atom. Possible intermediate products are 3,4-compounds of an acetylenic character (I) which under the influence of the catalyst isomerize to identified compounds with an allenic grouping of double bonds (II) or enter into reaction with the original hydrocarbon. The latter process accounts for the formation of considerable amounts of high-boiling products with the general formula $(CH_3)_3C-(C_6H_8)x$-Hal, where $\underline{x}$ = 2, 3, etc. Reaction in this direction is actually favored by the fact that initially formed acetylenic halides of the propargyl type have a higher reactivity than the original tertiary alkyl halides.

Increase in the excess of hydrocarbon leads to a slight increase in the yield of 1:1 addition products. Evidently higher products are also formed as a result of participation in the reaction of more than one multiple bond. It must also be mentioned that the addition of alkyl halides to vinylethylacetylene goes very much more slowly than under similar conditions with vinylacetylene. A special experiment established that a small amount of reaction product is formed in the course of 2 weeks. After 1 1/2 months there still remained a small amount of the original substance (which had been taken in excess).

Reaction of vinylethylacetylene with alkyl halides may be expected to lead to 6 addition products in 1:1 ratio:

$$C_2H_5-C\equiv C-CHHal-CH_2-C(CH_3)_3 \quad (I)$$

$$C_2H_5-CHal=C=CH-CH_2-C(CH_3)_3 \quad (II)$$

$$C_2H_5-C\equiv C-\underset{\substack{|\\ C(CH_3)_3}}{CH}-CH_2Hal \quad (III)$$

$$C_2H_5-\underset{\substack{|\\ C(CH_3)_3}}{C}=CHal-CH=CH_2 \quad (IV)$$

$$C_2H_5-\underset{\substack{|\\ C(CH_3)_3}}{C}=C=CH-\dot{C}H_2Hal \quad (V)$$

$$C_2H_5-CHal=\underset{\substack{|\\ C(CH_3)_3}}{C}-CH=CH_2 \quad (VI)$$

The structure of the prepared products was confirmed by ozonization. Cleavage with ozone of the product of addition of tertiary butyl chloride to vinylethylacetylene gave propionic and tertiary butylacetic acids. The products of ozonization did not include halogen-containing acids or carbonyl compounds. Formula (II) was therefore assigned to the substance.

Ozonic decomposition of the product of addition of tertiary butyl bromide to vinylethylacetylene likewise gave propionic and tertiary butylacetic acids. Bromoacetic acid was absent from the oxidation products. The fraction of acids with the highest boiling point was a bromine-containing acid, evidently α-bromo-γ-dimethylvaleric acid. On the basis of these data we concluded that the investigated substance is the allenic bromide (II) slightly contaminated with the acetylenic compound (I).

Such a structure of the prepared halides is confirmed by their behavior towards alcoholic alkali. On boiling the chloride with 10% alcoholic KOH for 1 hour, only 9.4% chlorine goes into solution. Under similar conditions the bromide loses 31% bromine.

Formation in both cases of trimethylacetic acid as the main product of oxidation provided conclusive proof that the radical adds on preferentially to the quaternary carbon atom of the conjugated system. Consequently, in the case of vinylalkylacetylenes, in contrast to the previously established rule, halogen derivatives do not add on in the same manner as hydrogen halides. Only in the case of hydrogen and hydrogen halides does the triple bond react at first. In the remaining cases that were investigated, the double bond is more reactive.

EXPERIMENTAL

1. Reaction of vinylethylacetylene with tertiary butyl chloride.

a) From 30 g (0.32 mole) of $(CH_3)CCl$ and 51 g (0.64 mole) of vinylethylacetylene* in the presence of 3 g of $ZnCl_2$, 0.3 ml of concentrated hydrochloric acid and 0.3 g of hydroquinone, we obtained 55 g of reaction products. The duration of the reaction was 46 days.

Upon vacuum-distillation, the substance was separated into the following fractions: 1st, 50-60° (2.5 mm), 10.3 g; 2nd, 100-120° (1.5 mm), 5.9 g; 3rd, 140-160° (1 mm), 3.6 g; residue – 33 g.

Repeated distillation of the 1st fraction yielded 8.2 g of product:
B.p. 72-73° (10 mm), d_4^{20} 0.9028, n_D^{20} 1.4737, MR_D 53.74. $C_{10}H_{17}Cl\,F_2$. Calc. 52.31
Found %: Cl 20.48. $C_{10}H_{17}Cl$. Calculated %: Cl 20.54.

When a weighed portion of the product (0.1765 g) was heated for 1 hour with a 10% alcoholic KOH solution, 9.4% (0.0034 g) of chlorine passed into the solution.

7.5 g of ozonides was obtained upon ozonation of 5.3 g of the substance. After decomposition of the ozonides, the ethereal extract did not contain carbonyl compounds (test with 2,4-dinitrophenylhydrazine in acetic acid). Propionic and tertiary butylacetic acids were isolated upon distillation of the obtained acids. Propionic acid (b.p. 140-143°) was purified through the sodium salt. The acid was dissolved in methanol and neutralized with a methanolic solution of NaOH. With addition of acetone, sodium propionate precipitated out. After 2-fold reprecipitation, the compound was dried at 150° and analyzed.

Found %: C 36.87; H 5.33; Na 24.45. $C_3H_5O_2Na$. Calculated %: C 37.53; H 5.25; Na 23.96.

The amide, m.p. 81°, and the anilide, m.p. 104°, were prepared from the salt by the usual methods.

Literature data [11] give: amide of propionic acid – m.p. 81.3°, anilide – m.p. 105°.

Tertiary butylacetic acid (boiling range 92-97° at 26 mm) also was purified through the sodium salt. The acid was neutralized by a solution of NaOH in methanol. The methanol was evaporated down to dryness. The residue was extracted with hot acetone (+0.5% H_2O). The crystals that came down from the acetone were again recrystallized from acetone (+0.5% H_2O).

Found %: C 52.48; H 8.16; Na 16.01. $C_6H_{11}O_2Na$. Calculated %: C 52.16; H 8.02; Na 16.15.

* It was prepared by the usual method [10].

From the salt we prepared the amide, m.p. 131.5°. A mixture test gave m.p. 131.5°. Literature data [12] give: m.p. 132°.

Not one of the acid fractions or the small residue from distillation contained halogen.

From the 2nd fraction a second distillation yielded 2.5 g of substance:

B.p. 110-115° (2 mm), d_4^{20} 0.9485, n_D^{20} 1.5013, MR_D 78.55. $C_{16}H_{25}Cl\,F_2\,F$. Calc. 78.03.
Found %: Cl 14.27. $C_{16}H_{25}Cl$. Calculated %: Cl 14.02.

Upon hydrolytic decomposition of a sample of the substance under the above described conditions, 14.5% chlorine passed into solution.

From the 3rd fraction we isolated 1.5 g of substance:

B.p. 145-155° (2 mm), d_4^{20} 0.9850, n_D^{20} 1.5153, MR_D 102.04. $C_{22}H_{33}Cl\,F_2\,F_2$. Calc. 103.63.
Found %: Cl 10.98. $C_{22}H_{33}Cl$. Calculated %: 10.65.

b) When the reaction was performed with another ratio of components: 66 g (0.72 mole) of $(CH_3)_3CCl$ and 40 g (0.5 mole) of vinylethylacetylene, we obtained 30 g of substance which upon fractionation, was separated into a fraction which boiled at 50-60° (2.5 mm), 4.8 g, and a residue of 24 g. From the 1st fraction we isolated a compound, b.p. 72-73° at 10 mm, d_4^{20} 0.9020, n_D^{20} 1.4728.

2. Reaction of vinylethylacetylene with tertiary butyl bromide.

45 g (0.33 mole) of $(CH_3)_3CBr$ and 53 g (0.66 mole) of vinylethylacetylene in the presence of 4.6 g of $ZnBr_2$, 0.2 g of concentrated hydrobromic acid and 0.2 g of hydroquinone were reacted for a period of 49 days and we obtained 55 g of reaction product. Vacuum-distillation at 50-70° (2 mm.) yielded 17.5 g of substance. Residue – 35 g.

A second distillation of the 1st fraction yielded 11 g of substance.

B.p. 86-88° (10 mm), d_4^{20} 1.1178, n_D^{20} 1.4973, MR_D 57.02. $C_{10}H_{17}Br\,F_2$. Calc. 55.20.
Found %: Br 36.42. $C_{10}H_{17}Br$. Calculated %: Br 36.80.

Upon hydrolytic decomposition under the above described conditions, 31% of bromine passed into solution (the sample weighed 0.2866 g; we found 0.0327 g of bromine ion).

Ozonization of 6.8 g of the substance yielded 9 g of ozonides. After the usual decomposition of the ozonides, the organic acids, extracted with ether, were separated by distillation into the following fractions: 1st, 140-145° (756 mm), 0.8 g; 2nd, 90-100° (26 mm), 1.9 g; 3rd, 100-130° (2 mm), 0.4 g; residue – 0.3 g.

The 1st and 2nd fraction did not contain halogen. From the 1st fraction, we isolated the sodium salt of propionic acid by the previously described method.

Found %: C 37.91; H 5.08; Na 24.21. $C_3H_5O_2Na$. Calculated %: C 37.53; H 5.25; Na 23.96.

From the 2nd acid fraction, we isolated the sodium salt of tertiary butylacetic acid.

Found %: C 51.79; H 8.00; Na 16.48. $C_6H_{11}O_2Na$. Calculated %: C 52.16; H 8.02; Na 16.15.

From the salt we prepared the amide of tertiary butylacetic acid, m.p. 131.5°. A test mixture melted at the same temperature. The 3rd acid fraction contained halogen. The sodium salt of this acid, prepared from methanol, was washed with anhydrous ether after the methanol had been evaporated off.

Found %: Br 33.36. $C_7H_{12}O_2BrNa$. Calculated %: Br 34.56.

All analyses for halogen were performed according to Prinasheim.

SUMMARY

1. The reaction of vinylethylacetylene with butyl chloride and bromide in presence of zinc halides was investigated.

2. It was shown that in both cases addition takes place with binding of the radical (the positively polarized portion of the molecule) at the terminal atom of the ethylenic bond, i.e. not at the same point as that of addition of hydrogen halides.

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ACTION OF ACETYL CHLORIDE AND ACETIC ANHYDRIDE UPON ALKYL ESTERS OF ARSENIOUS ACID

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In the preceding investigation [1] one of us studied the action of acetyl chloride and acetic anhydride upon some alkyl esters of α-methoxypropylene glycol arsenious acid. It was found that the reaction with acetyl chloride goes with formation of the acid chloride of α-methoxypropylene glycol arsenious acid without rupture of the ring; with acetic anhydride the product is the monoacetyl derivative of α-methoxypropylene glycol arsenious acid.

Continuing the investigation, we have studied the reaction of acetyl chloride and anhydride with the simplest alkyl esters of arsenious acid. By the action of 1 mole acetyl chloride on 1 mole ester of arsenious acid, the reaction goes with slight heat development according to the equation:

$$(RO)_3As + CH_3COCl \longrightarrow (RO)_2AsCl + CH_3COOR.$$

In our experiments we isolated six acid chlorides of dialkyl arsenious acids (Table 1).

TABLE 1

Preparation No.	Formula	Boiling point at pressure (mm)	d_4^{20}	n_D^{20}	Content in %			
					As		Cl	
					found	calc.	found	calc.
1	C_2H_5O, C_3H_7O >AsCl . . .	72—73° (10)	1.2987	1.4672	34,19	34.92	16.57	16.87
2	n-$(C_3H_7O)_2AsCl$ . .	73—75 (10)	1.2447	1.4683	32.67	32.47	15.91	15.51
3	n-C_3H_7O, n-C_4H_9O >AsCl . .	96—96.5(14)	1.2280	1.4630	30.86	30.88	14.33	14.62
4	iso-$(C_4H_9O)_2AsCl$.	108—111 (25)	1.2276	1.4639	29.73	29.39	—	—
5	n-$(C_4H_9O)_2AsCl$ . .	110—112 (10)	1.2401	1.4569	29.29	29.39	—	—
6	n-$(C_6H_{13}O)_2AsCl$.	140—143 (2)	1,0960	1.4642	23.71	23.96	11.09	11.34

The prepared acid chlorides of dialkylarsenious acids are colorless, readily mobile liquids. They are easily hydrolyzed by atmospheric moisture with formation of arsenic trioxide; they react with hydrogen sulfide to give a yellow precipitate. Our attempt to obtain dialkyl arsenious acids by saponification of equimolar amounts of the acid chlorides with water did not meet with success. In its general form the saponification reaction may be represented by the equation:

$$2(RO)_2AsCl + 3HOH \longrightarrow As_2O_3 + 4ROH + 2\ HCl.$$

Acid chlorides readily enter into reaction with alcohols in presence of anhydrous pyridine with formation of mixed esters of arsenious acid. In this manner we synthesized ethyl-dipropyl, ethyl-dibutyl and propyl-dibutyl

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esters of arsenious acid. The mixed esters react with acetyl chloride to form asymmetrical acid chlorides, alkoxy groups being replaced by chlorine according to the following scheme:

$$\begin{matrix} C_2H_5O \\ C_3H_7O \end{matrix}\!\!>As-OC_3H_7 + CH_3-COCl \longrightarrow \begin{matrix} C_2H_5O \\ C_3H_7O \end{matrix}\!\!>AsCl + CH_3-COOC_3H_7.$$

We also studied the interaction of alkyl esters of arsenious acid with acetic anhydride. Our experiments showed that these alkyl esters, when heated with acetic anhydride, form mixed anhydrides of dialkyl arsenious and acetic acids according to the scheme:

$$(RO)_3As + \begin{matrix} CH_3-CO \\ CH_3-CO \end{matrix}\!\!>O \longrightarrow \begin{matrix} (RO)_2As \\ CH_3-CO \end{matrix}\!\!>O + CH_3-COOR.$$

Some data for these mixed anhydrides are presented in Table 2.

The separated mixed anhydrides are colorless liquids which are unstable in the air, undergoing hydrolysis with formation of a white precipitate of arsenic trioxide.

TABLE 2

No.	Formula	Boiling point at pressure (mm)	d_4^{20}	n_D^{20}	Content in %	
					found	calc.
1	iso-$(C_4H_9O)_2As-O-CO-CH_3$	111—112° (12)	1.1554	1.4420	26.45	26.69
2	n-$(C_4H_9O)_2As-O-CO-CH_3$	125—126 (10)	1.1803	1.4483	26.74	26.69
3	n-$(C_6H_{13}O)_2As-O-CO-CH_3$	146—148 (5)	1.0954	1.4520	22.46	22.29

In view of the latter reaction, it was of interest to study the reaction of acetic acid with alkyl esters of arsenious acid. Our experiments established that reaction of 1 mole acetic acid with 1 mole of aliphatic arsenite at elevated temperature led to formation of alkyl acetates, mixed anhydrides of dialkyl arsenious and acetic acids, arsenic trioxide and the corresponding alcohols. Formation of these substances may be represented by the following series of reactions:

$$(RO)_3As + CH_3COOH \longrightarrow (RO)_2AsOCOCH_3 + ROH,$$

$$ROH + CH_3COOH \rightleftharpoons CH_3COOR + H_2O,$$

$$2(RO)_2As-OCOCH_3 + 3H_2O \longrightarrow As_2O_3 + 2CH_3COOH + 4ROH,$$

$$(RO)_3As + 3H_2O \rightleftharpoons 6ROH + As_2O_3.$$

EXPERIMENTAL

The initial substances, i.e. alkyl esters of arsenious acid, were prepared by heating arsenious acid anhydride with the corresponding alcohols. Certain data on them are given in Table 3.

Preparation of mixed esters of arsenious acid. 30 g of ethoxydichloroarsine was added through a dropping funnel, with cooling, to a mixture of 19 g of n-propyl alcohol, 25 g of anhydrous pyridine and 250 ml of ethyl ether. The precipitate was filtered off and washed with ether. After the ether was driven off on a water bath, the remaining mass was distilled through a Widmer column in vacuum. Yield 12.1 g (31.9%). The ethyl-di-n-propyl ester of arsenious acid was a colorless light-refracting liquid:

B. p. 92-93° (19 mm), d_4^{20} 1.1325, n_D^{20} 1.4423, MR_D 54.51; calc. 54.89.

Found %: As 31.14. $C_8H_{19}O_3As$. Calculated %: As 31.45.

In this way we synthesized the ethyldibutyl and propyldibutyl esters of arsenious acid. Certain data on these esters are given in Table 4.

TABLE 3

No.	Formula	Boiling point at pressure (mm)	d_4^{20}	n_D^{20}	Content As (in %)	
					found	calc.
1	n-$(C_3H_7O)_3As$	97—98° (13)	1.1132	1.4391	29.70	29.71
2	iso-$(C_4H_9O)_3As$	116—117 (12)	1.0568	1.4390	25.60	25.76
3	n-$(C_4H_9O)_3As$	109 (4)	1.0683	1.4428	25.54	25.76
4	n-$(C_6H_{13}O)_3As$	159 (2)	1.0119	1.4502	20.03	19.70

TABLE 4

Preparation number	Formula	Boiling point at pressure (mm)	d_4^{20}	n_D^{20}	Content As (in %)	
					Found	Calculated
1	$C_2H_5OAs(OC_4H_9)_2$	110-113° (9)	1.1262	1.4542	28.48	28.14
2	n-$C_3H_7OAs(OC_4H_9)_2$	112-112.5 (14)	1.0930	1.4438	26.83	26.73

Preparation of a di-n-propylarsenious acid chloride. 20 g of n-tripropylarsenite and 6.2 g of acetyl chloride were placed in a Arbuzov distilling flask. The temperature of the liquids rose from 19 to 33° upon mixing. The reaction mixture was further heated to 110° in the course of 30 minutes. The reaction products were distilled: 1st fraction, up to 50° (13 mm), 6.5 g, n_D^{20} 1.3852, was propyl acetate; 2nd fraction 73-75° (10 mm), 13.8 g, d_4^{20} 1.2447, n_D^{20} 1.4683 — was a colorless readily hydrolyzed liquid.

Found %: As 32.67, 32.36; Cl 15.91; MR_D 49.15. $C_6H_{14}O_2ClAs$. Calculated %: As 32.47; Cl 15.51; MR_D 48.85.

Preparation of ethyl-n-propylarsenious acid chloride. 15.4 g of ethyl-di-n-propylarsenite and 5 g of acetyl chloride were taken. Upon combination the temperature of the liquids rose to 43°. The contents of the flask were further heated on an oil bath for 10 hours. The next day, the contents were distilled. The following two fractions were separated:

1st, b.p.101-102°, n_D^{20} 1.3828, which corresponded to propyl acetate; 2nd, b.p. 72-73° (10 mm) — a colorless liquid, d_4^{20} 1.2987, n_D^{20} 1.4672.

Found %: As 34.49; Cl 16.57. $C_5H_{12}O_2ClAs$. Calculated %: As 34.94; Cl 16.53.

The other two dialkylarsenious acid chlorides were prepared by the above method, by reacting equimolecular quantities of trialkylarsenite and acetyl chloride.

Preparation of mixed anhydride of dibutylarsenious and acetic acids. A mixture of 20 g of tributyl ester of arsenious acid and 6.8 g of acetic anhydride was heated on an oil bath at 140-146° for 7 hours. Vacuum-distillation yielded the following fractions: 1st, up to 30° (20 mm), 7.6 g and 2nd, 125-126° (10 mm), 14.2 g. After distillation, from the 1st fraction we isolated pure butyl acetate, b.p. 125° and n_D^{20} 1.3944, 7.1 g. A second distillation of the 2nd fraction yielded a substance with the same boiling point; d_4^{20} 1.1803, n_D^{20} 1.4483.

Found %: As 26.59, 26.72. $C_{10}H_{21}O_4As$. Calculated %: As 26.69.

The analytical data for arsenic showed that the isolated compound was the mixed anhydride of dibutylarsenious and acetic acids.

The synthesis for the other mixed anhydrides of composition $(RO)_2AsOCOCH_3$ is the same as the one described above.

Action of Acetic Acid on Trialkylarsenites

Experiment 1. 13 g of n-propyl ester of arsenious acid and 3 g of glacial acetic acid were heated on an oil bath to the boiling point for 30 minutes. The reaction proceeded with evolution of arsenious acid anhydride. Distillation yielded 6 g of a fraction that boiled at 96-102° (theoretical yield 5.5 g). After a second distillation, we isolated a compound, b.p. 101-101.5°, n_D^{20} 1.3846, which corresponded to n-propyl acetate. Later, upon vacuum-distillation, we isolated a fraction, b.p. 103° (10 mm), n_D^{20} 1.4440.

Found %: As 29.68, 29.90. $C_8H_{17}O_4As$. Calculated %: As 29.73.

The analytical data for arsenic showed that the compound was the mixed anhydride of dipropylarsenious acids. However, it must be noted that determination of the acetyl group gave contradictory results: instead of 19.61 mg, we found 11.62 mg.

Experiment 2. A mixture of 11.3 g of n-hexyl arsenite and 1.8 g of acetic acid was heated to 120° for 40 minutes. During this reaction, a white precipitate of arsenic trioxide separated out. Vacuum-distillation yielded two fractions: 1st, b.p. 62° (16 mm), n_D^{20} 1.4170, and 2nd, b.p. 153° (2 mm), n_D^{20} 1.4510.

The 1st fraction was redistilled: b.p. 169° (760 mm), which corresponded to n-hexyl acetate. We could not isolate a single compound in its pure state from the 2nd fraction.

Hydrolysis of dibutylarsenious acid chloride. 3 g of dibutylarsenious acid chloride was mixed with 45 ml of water. The hydrolysis reaction proceeded very vigorously with the formation of a white precipitate. The precipitate was filtered off, washed and dried to constant weight.

Found %: As 75.41. As_2O_3. Calculated %: As 75.73.

Action of hydrogen sulfide on di-n-propylarsenious acid chloride. Dry hydrogen sulfide was passed into a solution of 2.3 g of the acid chloride in 40 ml of absolute ether. The reaction evolved heat and a yellow precipitate formed. The further course of the reaction was described in the literature [2]. The weight of the arsenic trisulfide obtained, was 1.18 g (96%).

SUMMARY

1. Reaction of equimolar amounts of acetyl chloride and alkyl esters of arsenious acids gave some acid chlorides of dialkyl arsenious acids. Their properties were studied.

2. It was shown that asymmetric acid chlorides are formed on reaction of acetyl chloride with mixed esters of arsenious acid.

3. Reaction of acetic anhydride with trialkyl arsenites gave mixed anhydrides of the general formula $(RO)_2AsOCOCH_3$ whose properties were studied.

4. It was shown that a complex reaction takes place between acetic acid and trialkyl arsenites with formation of alkyl acetates of the mixed anhydrides, arsenic trioxide and the corresponding alcohols.

5. An attempt to prepare dialkyl arsenious acids by hydrolysis of the corresponding acid chlorides was unsuccessful.

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TERTIARY TRIHYDRIC ALCOHOLS OF THE ACETYLENIC SERIES AND THEIR TRANSFORMATIONS

IX. DEHYDRATION OF 2-METHYL-5-(1-HYDROXYCYCLOHEXYL)-HEXYNE-3-DIOL-2,5-AND 2,4-DI-(1-HYDROXYCYCLOHEXYL)-BUTYNE-3-OL-2

V. I. Nikitin and A. Kh. Khamatov

In preceding communications [1] we described the dehydration of 2,3,6-trimethylheptyne-4-triol-2,3,6 and of 3,4,7-trimethyloctyne-5-triol-3,4,7 with 20% sulfuric acid, potassium bisulfate and p-toluenesulfonic acid. Dehydration was shown to proceed preferentially with formation of α-glycols of the isopropenylacetylene series in yields of 60-70%. Concurrently dehydration of the triols also proceeds to a smaller extent (4-8%) with loss of two molecules of water and formation of dienynic carbinols.

In the present investigation our objective was the clarification of the influence of cyclic radicals, introduced into the molecule of an acetylenic triol, on the character of the dehydration reaction. For this purpose we subjected 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (I) and 2,4-di-(1-hydroxycyclohexyl)-butyne-3-ol-2 (IX) to the action of dehydrating agents. These two compounds were synthesized for the first time by one of us and S. D. Savranskaya [2].

2-Methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (I) was subjected to the action of 20% sulfuric acid, potassium bisulfate and p-toluenesulfonic acid. In each case we were able to isolate two compounds: an α-glycol of the isopropenylacetylene series – 2 methyl-5-(1-hydroxycyclohexyl)-hexene-1-yn-3-ol-5 (II), and a dienynol – 2-methyl-5-(1-hydroxycyclohexyl)-hexadien-1,5-yne-3 (III):

The yield of the enynediol (II) on dehydration both with sulfuric acid and potassium bisulfate was only 10%; that of dienynol (II) was 48% with sulfuric acid and 26% with potassium bisulfate. On carrying out the dehydration with p-toluenesulfonic acid, however, the yield of the enynediol (II) rose to 26% and that of the dienynol (III) was 25% calculated on the original acetylenic triol. In all cases the dehydration of the triol is accompanied by considerable resinification of the reaction products.

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The structure of glycol (II) was verified by oxidation with potassium permanganate; this reaction gave cyclohexanone, acetylcyclohexanol and formic, acetic and oxalic acids.

Hydrogenation of glycol (III) both over platinum and palladium catalyst in methanol solution proceeds violently, but after addition of 2 moles hydrogen the rate of addition of hydrogen slows down appreciably. On introducing the calculated amount of hydrogen (2 moles) we obtained the ethylenic glycol, 2-methyl-5-(1-hydroxycyclohexyl)-hexen-2-ol-5 (IV).

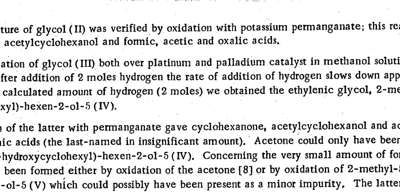
Oxidation of the latter with permanganate gave cyclohexanone, acetylcyclohexanol and acetic, oxalic, adipic and formic acids (the last-named in insignificant amount). Acetone could only have been formed from 2-methyl-5-(1-hydroxycyclohexyl)-hexen-2-ol-5 (IV). Concerning the very small amount of formic acid, this might have been formed either by oxidation of the acetone [8] or by oxidation of 2-methyl-5-(1-cyclohexyl)-hexen-1-ol-5 (V) which could possibly have been present as a minor impurity. The latter route is more probable.

Exhaustive hydrogenation of glycols (II) and (IV) in glacial acetic acid solution led to the saturated glycol, 2-methyl-5-(1-hydroxycyclohexyl)-hexanol-5 (VI).

The structure of the dienynic alcohol (III) was confirmed by oxidation with potassium permanganate, which led to formic, acetic, oxalic and α-hydroxyhexahydrobenzoic acid. Hydrogenation of the dienynol (III) leads to absorption of 4 moles hydrogen with formation of 2-methyl-5-(1-hydroxycyclohexyl)-hexane (VII).

Under the action of 25% sulfuric acid, the saturated glycol (VI) does not undergo the pinacoline rearrangement but is dehydrated with loss of two molecules of water and formation of a diene hydrocarbon which in all probability is 2-methyl-5-(1-cyclohexenyl)-hexene-4 (VIII).

The action of dehydratingagents upon 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 (IX) is entirely different. No reaction products could be isolated after treatment with 5, 10, 20 or 30% sulfuric acid or with potassium bisulfate. The acid and the bisulfate once again had a great destructive action on the molecule to the accompaniment of marked resinification. Even p-toluenesulfonic acid is such a strong dehydrating agent for this acetylenic glycerol that the main reaction product is a dienic carbinol — 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-buten-1-yne-3 (X) in yield of 40%, while the yield of glycol, 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-butyn-3-ol-2 (XI), does not exceed 1%.



The amount of glycol (XI) was too small for oxidation, but on the basis of analysis we can infer, by analogy with the preceding cases of dehydration, that its structure is that of an α-glycol. It absorbs 3 moles hydrogen in exhaustive hydrogenation and gives a saturated glycol — 2-(1-hydroxycyclohexyl)-4-cyclohexylbutanol-2 (XII).

The structure of 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-buten-1-yne-3 (X) was confirmed by permanganate oxidation, which gave cyclohexanone and formic, oxalic and adipic acids. Judging by this result, the dienynol can be assigned the structure of either 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-buten-1-yne-3 (X) or of 2-(cyclohexenyl-1)-4-(1-hydroxycyclohexyl)-buten-1-yne-3. In view of the fact that hydroxyls adjacent to a triple bond are more labile, as confirmed by the investigations of many chemists [3-7] and by our studies [1], we regard structure (X) as the more probable one for this dienynol.

On hydrogenation, the dienynol (X) takes up 4 moles hydrogen to form the saturated alcohol, 2-(1-hydroxycyclohexyl)-4-cyclohexylbutane (XIII).

EXPERIMENTAL

2-Methyl-5-(hydroxycyclohexyl)-hexyne-3-diol-2,5 was prepared by the previously described method of condensing dimethylacetylenylcarbinol with acetylcyclohexanol [2]. B.p. 151-155° (3 mm), m.p. 87-88°.

1. Dehydration of 2-Methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (I)

With sulfuric acid. A mixture of 20.5 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 and 150 ml of 20% sulfuric acid was heated on a boiling water bath for 2 hours. A violet-colored oily product separated out, was extracted with ether, treated with dilute soda solution, dried with sodium sulfate and after the ether was driven off, it was vacuum-distilled at 3 mm. We obtained fractions: 1st, b.p. 100-103°, 8.8 g, crystals, m.p. 47-48° (from petroleum ether), was 2-methyl-5-(1-hydroxycyclohexyl)-hexadien-1,5 yne-3 (III); 2nd, b.p. 120-125°, 2 g, crystals, m.p. 74-75° (from benzene), was 2-methyl-5-(1-hydroxycyclohexyl)-hexen-1-yn-3-ol-5 (II); 3rd, b.p. 150-155°, 2.2 g, m.p. 87-88° — initial substance; resinified residue of 6.4 g.

With potassium bisulfate. A mixture of 18.7 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 with 6 g of finely ground potassium bisulfate and 0.1 g of pyrogallol was heated over a bath to 140-145° in 4 mm vacuum. At 110-125°, 12.4 g of substance was distilled off. The crude product was dissolved in ether, dried with sodium sulfate and after the ether was driven off, it was vacuum-distilled at 3 mm: 1st fraction, boiled at 100-103°, 4.7 g, crystals, m.p. 47-48°; 2nd fraction boiled at 100-125°, 1.9 g, crystals, m.p. 74-75°; resinified residue of 3.5 g.

With p-toluenesulfonic acid. 25 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 was heated with 5 mg of p-toluenesulfonic acid to 165-170° in 7-8 mm vacuum. At 145-150°, 17.7 g of substance distilled off. The reaction products were dissolved in ether, dried with sodium sulfate, and after the ether was driven off, they were vacuum-distilled at 3 mm: 1st fraction boiled at 100-103°, 6.2 g, crystals, m.p. 47-48°; 2nd fraction boiled at 120-125°, 6.5 g, crystals, m.p. 74-75°.

Analysis of 2-Methyl-5-(1-hydroxycyclohexyl)-hexadien-1,5-yne-3 (III)

Found %: C 81.93, 81.98; H 9.98, 9.54; OH 9.7, 9.4. $C_{13}H_{18}O$. Calculated %: C 82.10; H 9.47; OH 9.0.

Oxidation. Drop-wise, in the course of 6 hours, 800 ml of 3% potassium permanganate solution was added, with mechanical stirring, to 4.4 g of methyl-(hydroxycyclohexyl)-hexadienyne (III) in 100 ml of water. When oxidation was complete, the manganese dioxide was filtered off and the filtrate was extracted with ether. After the ether was driven off, there were no neutral products. The filtrate was then acidified with hydrochloric acid and the volatile acids were driven off with steam. It took 245.5 ml of 0.1 N KOH solution to neutralize 1000 ml of volatile acid distillate. The solution of the volatile acid salts was evaporated down almost to dryness. Qualitative reactions established the presence of formic acid by the calomel test and of acetic acid — by the cacodyl test. After the volatile acids were distilled off, the solution was neutralized with alkali and oxalic acid was precipitated with $CaCl_2$ in the form of calcium oxalate. The precipitate was filtered off, dissolved in hydrochloric acid and extracted with ether in an extractor. After the ether was driven off, we isolated 1.9 g of oxalic acid, m.p. 101-102°, which was identified by a mixture test. After precipitation of the oxalic acid, the filtrate was acidified with hydrochloric acid and extracted in an extractor. After the ether was driven off, we isolated 0.6 g of α-hydroxyhexahydrobenzoic acid, m.p. 105-106° (from benzene). A mixture test of the product with α-hydroxyhexahydrobenzoic acid melted at 105-106°.

Thus, upon oxidation of 2-methyl-5-(1-hydroxycyclohexyl)-hexadien-1,5-yne-3, we isolated formic, acetic, oxalic and α-hydroxyhexahydrobenzoic acid.

Hydrogenation. 10 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexadien-1,5-yne-3 (III) dissolved in 60 ml of anhydrous methanol was hydrogenated over platinum oxide (according to Adams) in the course of 7 hours. 5.6 liters of hydrogen was absorbed (22°, 698 mm). 5.53 liters of hydrogen was calculated on the basis of 4 moles.

After the methanol was driven off, vacuum-distillation yielded 8.5 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexane (VII); b.p. 100-102° (3 mm).

d_4^{20} 0.9150, n_D^{20} 1.4784, MR_D 61.31; calc. 61.56.

Found %: C 78.79, 78.56; H 13.16, 13.13; OH 8.41, 8.65. $C_{13}H_{26}O$. Calculated %: C 78.79; H 13.13; OH 8.58.

Analysis of 2-Methyl-5-(1-hydroxycyclohexyl)-hexen-1-yn-3-ol-5 (II)

Found %: C 74.63, 74.87; H 9.63, 9.69; OH 16.59, 16.4. $C_{13}H_{20}O_2$. Calculated %: C 74.94; H 9.6; OH 16.35.

Oxidation. 1200 ml of 3% potassium permanganate solution was slowly added, drop-wise, with mechanical stirring, in the course of 7 hours, to 11.9 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexen-1-yn-3-ol-5 (II) in 100 ml of water. Separation and analysis of the products were performed in the same manner as in the preceding experiment.

We separated 1.9 g of neutral substances, m.p. 150-155° (690.8 mm), which with semicarbazide gave a mixture of semicarbazones of cyclohexanone and acetylcyclohexanol. Utilizing their different solubilities in benzene, we were able to separate them; after several recrystallizations from methanol, the soluble portion melted at 164-165° and corresponded to the semicarbazone of cyclohexanone (mixture test). After recrystallization from methanol, the portion that was insoluble in benzene melted at 194-195°. A mixture test with the semicarbazone of acetylcyclohexanol gave no depression. From the acids we isolated formic and acetic acids, 3.5 g (their presence was proved qualitatively by the formation of calomel and cacodyl oxide), and oxalic acid, 1.2 g, m.p. 101-102° (mixture test).

Thus, oxidation of 2-methyl-5-(1-hydroxycyclohexyl)-hexen-1-yn-3-ol-5 yielded cyclohexanone, acetylcyclohexanol and formic, acetic and oxalic acids.

Hydrogenation. 11 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexen-1-yn-3-ol-5 (II), dissolved in 75 ml of anhydrous methanol, was hydrogenated over palladium supported on chalk, in the course of 8 hours. After 2.7 liters of hydrogen (22°, 698.6 mm) had been absorbed, hydrogenation almost stopped. 2.75 liters of hydrogen was calculated on the basis of 2 moles. After the methanol was driven off, the hydrogenated product was vacuum-distilled, yield 9.4 g, b.p. 120-122° (3 mm), which was the ethylenic glycol — 2-methyl-5-(1-hydroxycyclohexyl)-hexen-2-ol-5 (IV).

d_4^{20} 0.9853, n_D^{20} 1.4908, MR_D 62.3. $C_{13}H_{24}O_2F$. Calc. MR_D 62.62.

Found %: C 73.45, 73.67; H 11.68, 11.24 ; OH 16.21, 16.07. $C_{13}H_{24}O_2$. Calculated %: C 73.58; H 11.32; OH 16.00.

Oxidation. 930 ml of 3% potassium permanganate solution was added, slowly, drop-wise, with stirring, in the course of 8 hours, to 14.1 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexen-2-ol-5 (IV) in 100 ml of water. Further analysis of the oxidation products was performed as in preceding cases.

Fractionation of the neutral products of oxidation yielded 0.8 g of acetone, b.p. 54-56°, which gave 2,4-dinitrophenylhydrazone, m.p. 126-127° (test mixture). After the acetone was driven off, the neutral products that remained in the solution were extracted in an extractor with ether. We obtained 5 g of crude product which, upon distillation, yielded: 1st fraction, b.p. 100-150° (694.1 mm), 0.5 g; 2nd fraction, b.p. 70-80° (6 mm), 1.5 g, n_D^{20} 1.4898.

The 1st fraction, which boiled at 100-150°, corresponded to cyclohexanone; the semicarbazone, m.p. 165-166°, gave no depression in a test mixture with the semicarbazone of cyclohexanone. The 2nd fraction which boiled at 70-80° (6 mm) gave a semicarbazone, m.p. 194-195°, which corresponded to the semicarbazone of acetylcyclohexanol (mixture test). The 3rd fraction, b.p. 118-120° (3 mm) proved to be the unoxidized initial compound.

From the volatile acids, we isolated 1.3 g of acetic acid, presence determined by the cacodyl test, and traces of formic acid; from the non-volatile acids — 1.7 g of oxalic acid, m.p. 101-102° (mixture test) and 1.2 g of adipic acid, m.p. 150-151° (mixture test).

Hydrogenation of 2-methyl-5-(1-hydroxycyclohexyl)-hexen-2-ol-5 (IV). 9.5 g of the substance, dissolved in 30 ml of glacial acetic acid, was hydrogenated over platinum oxide in the course of 6 hours. 1.2 liters

of hydrogen (20.5°, 693.4 mm) was absorbed. 1.18 liters was calculated on the basis of 1 mole. The acetic acid was neutralized with soda, the hydrogenated product was extracted with ether and dried with sodium sulfate. After the ether was driven off, the product was vacuum-distilled. We isolated 8.2 g of 2-methyl-5-(hydroxycyclohexyl)-hexanol-5 (VI).

B. p. 115-117° (2.5 mm), d_4^{20} 0.9707, n_D^{20} 1.4820, MR_D 62.84. $C_{13}H_{26}O_2$. Calc. 63.08.

Found %: C 72.56, 72.73; H 12.10, 12.13; OH 15.96, 16.18. $C_{13}H_{26}O_2$. Calculated %: C 72.90; H 12.15; OH 15.89.

Dehydration of 2-methyl-5-(1-hydroxycyclohexyl)-hexanol-5 (VI)

With sulfuric acid. A mixture of 10 g of the substance and 100 ml of 25% sulfuric acid was heated on a boiling water bath for 2 hours. After the usual separation of the reaction products, we isolated 7 g of substance, b.p. 115-117° (2.5 mm), n_D^{20} 1.4820, which was the unchanged initial substance. There was 2.5 g of resinified residue.

With potassium bisulfate. A mixture of 8 g of substance and 1.7 g of finely pulverized potassium bisulfate was heated on a bath to 140° in 12 mm vacuum. 5 g of substance distilled off at 110-115°. After a second distillation, we isolated 4.2 g of substance b.p. 112-114° (12 mm) which was in all probability 2-methyl-5-(1-hydroxycyclohexenyl)-hexene-4 (VIII).

d_4^{20} 0.8812, n_D^{20} 1.4985, MR_D 59.26. $C_{13}H_{22}F_2$. Calc. 59.1.

Found %: C 87.64, 87.34; H 12.28, 12.20. $C_{13}H_{22}$. Calculated %: C 87.64; H 12.36. We found no carbonyl or hydroxyl groups present.

Hydrogenation. 0.4914 g of Compound (VIII) in 25 ml of anhydrous methanol was hydrogenated over platinum oxide in the course of 2 hours. 146 ml of hydrogen was absorbed (24°, 689.2 mm). 148.5 ml hydrogen was calculated on the basis of 2 moles.

II. Dehydration of 2,4-Di-(1-hydroxycyclohexyl)-butyn-3-ol-2 (IX)

2,4-Di-(1-hydroxycyclohexyl)-butyn-3-ol-2 was prepared by the previously described method of condensing acetylenylcyclohexanol with acetylcyclohexanone [2], m.p. 107-109°.

Upon heating it on a water bath (60-70°) with 50 and 20% sulfuric acid solution, and also, upon distilling it in vacuum (6-7 mm) at 150-170° in the presence of anhydrous potassium bisulfate, complete resinification occurred and no reaction products could be isolated.

p-Toluenesulfonic acid. A mixture of 20 g of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 (IX) and 5 mg of a mixture of substances, b.p. 150-160°, distilled off. The reaction products were dissolved in ether, dried with sodium sulfate and after the ether was driven off, they were vacuum-distilled at 2 mm: 1st fraction, b.p. 148-150°, 8.6 g, 2nd fraction, b.p. 160-170°, 2.6 g.

Upon standing, 0.3 g of crystals, m.p. 114-115° (from benzene) came down in the 1st fraction; they proved to be ionenediol — 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-butyn-3-ol-2 (XI). A second distillation of the liquid portion of the 1st fraction yielded 8.2 g of substance, b.p. 134-135° (1 mm), which was 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-buten-1-yne-3 (X). The 2nd fraction, b.p. 160-170° (2 mm), was the initial product, m.p. 107-108° (from benzene).

Analysis of 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1) buten-1-yne-3 (X)

B.p. 134-135° (1 mm), d_4^{20} 1.023, n_D^{20} 1.5555, MR_D 72.21. $C_{16}H_{22}OF_2$. Calc. 70.21.

Found %: C 83.45, 83.54; H 9.72, 9.60; OH 7.31, 7.35. $C_{16}H_{22}O$. Calculated %: C 83.49; H 9.57; OH 7.39.

Oxidation. 940 ml of 3% potassium permanganate solution was added slowly, drop-wise, in the course of 6 hours, to 8.8 g of hydroxycyclohexylcyclohexenylbutenyne (X) in 100 ml H_2O. Further analysis of the oxidation products was performed as in the preceding cases of oxidation. We obtained 4 g of neutral substances from which we separated a fraction, b.p. 140-150°, which gave a semicarbazone, m.p. 165-166°, corresponding to that of cyclohexanone (mixture test).

In the volatile acid distillate we detected only formic acid (calomel test), which consumed 34 ml 1 N KOH solution for neutralization, which corresponded to 0.16 g of formic acid. From the non-volatile acids, we isolated 0.5 g of oxalic acid, m.p. 101-102° (mixture test) and 2 g of adipic acid, m.p. 150-151° (mixture test).

Thus, oxidation of 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)buten-1-yne-3 (X) yielded cyclohexanone and formic, oxalic, and adipic acids.

Hydrogenation. 11.3 g of hydroxycyclohexylcyclohexenylbutenyne (X) in 75 ml of anhydrous methanol was hydrogenated over platinum oxide in the course of 8 hours. 5.250 liters of hydrogen (20°, 689.4 mm) instead of the calculated 5.208 liters (4 moles). After the methanol was driven off, the hydrogenated product was vacuum-distilled and we isolated 8.7 g of a substance which was 2-(1-hydroxycyclohexyl)-4-cyclohexylbutane (XIII):

B.p. 148-149° (3 mm), d_4^{20} 0.9661, n_D^{20} 1.5030, MR_D 72.83. $C_{16}H_{30}O$. Calc. 73.2.

Found %: C 80.46, 80.52; H 12.53, 12.49; OH 7.30, 7.21. $C_{16}H_{30}O$. Calculated %: C 80.67; H 12.60; OH 7.13.

Analysis of 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)butyn-3-ol-2 (XI)

Found %: C 77.45, 77.41; H 9.59, 9.50; OH 13.73, 13.81. $C_{16}H_{24}O_2$. Calculated %: C 77.41; H 9.68; OH 13.71.

Hydrogenation. 1.7 g of hydroxycyclohexylcyclohexenylbutynol (XI) in 25 ml of anhydrous methanol was hydrogenated over platinum oxide in the course of 8 hours. 570 ml of hydrogen (27°, 685.4 mm) was absorbed (561.1 ml calculated on the basis of 3 moles). After the methanol was driven off, 2-(1-hydroxycyclohexyl)-4-cyclohexylbutanol-2 (XII) formed, was recrystallized from benzene and melted at 106-107°.

Found %: C 79.43, 79.32; H 11.69, 11.76; OH 13.41, 13.22. $C_{16}H_{30}O_2$. Calculated %: C 79.53; H 11.81; OH 13.39.

SUMMARY

1. Dehydration of 2-methyl-5-(1-hydroxycyclohexyl)-hexyn-3-diol-2,5 (I) goes in two directions: with formation of an α-glycol – 2-methyl-5-(1-hydroxycyclohexyl)-hexen-1-yn-3-ol-5 (II), and a dienynic carbinol – 2-methyl-5-(hydroxycyclohexyl)-hexadien-1,5-yne-3 (III). In presence of sulfuric acid or of potassium bisulfate the main reaction product is the dienynic carbinol, while with p-toluenesulfonic acid both products are obtained in nearly equal quantities.

2. Hydrogenation of the α-glycol, 2-methyl-5-(1-hydroxycyclohexyl)-hexen-1-yn-3-ol-5 (II), over platinum and palladium catalysts slows down abruptly after absorption of 2 moles hydrogen. An ethylenic glycol, 2-methyl-5-(1-hydroxycyclohexyl)-hexen-2-ol-5 (IV) is obtained, which in acetic acid solution in presence of platinum catalyst is hydrogenated to 2-methyl-5-(1-hydroxycyclohexyl)-hexanol-5 (VI).

3. 2-Methyl-5-(1-hydroxycyclohexyl)-hexanol-5 (VI) does not undergo the pinacoline rearrangement under the action of 20% sulfuric acid but is dehydrated to a dienic hydrocarbon, apparently 2-methyl-5-(cyclohexenyl-1)-hexene-4 (VIII).

4. Dehydration of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 (IX) with 5, 10, 20, or 30% sulfuric acid or with potassium bisulfate is accompanied by resinification; p-toluenesulfonic acid dehydrates it with formation principally of a dienynic glycol – 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-buten-1-yne-3 (X), while the yield of α-glycol, 2-(1-hydroxycyclohexyl)-4-(cyclohexenyl-1)-butyn-3-ol-2 (XI), is insignificant.

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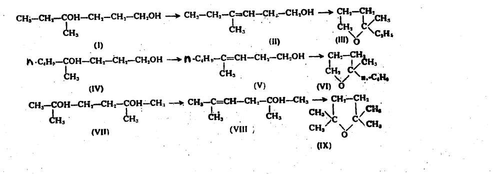
THE MECHANISM OF DEHYDRATION OF γ-GLYCOLS

II. STUDY OF THE DEHYDRATION OF 2,5-DIMETHYLHEXANEDIOL-2,5; 4-METHYLHEXANEDIOL-1,4, AND 4-METHYLOCTANEDIOL-1,4

T. A. Favorskaya and N. P. Ryzhova

It has been shown by one of us and O. V. Sergievskaya [1] that the primary product of dehydration of 2-methylpentanediol-2,5 is an unsaturated alcohol, 2-methylpenten-2-ol-5, which then isomerizes to 2,2-dimethyltetrahydrofuran.

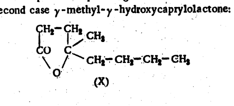
In the present work we established that also other primary-tertiary γ-glycols containing aliphatic radicals – 4-methylhexanediol-1,4 (I) and 4-methyloctanediol-1,4 (IV) – are dehydrated by the same mechanism as that for the ditertiary γ-glycol, 2,5-dimethylhexanediol-2,5 (VII).



Distillation of these glycols with sulfuric acid solution (pH 1.6) gave the unsaturated alcohols: 4-methylhexen-3-ol-1 (II); 4-methyloctene-3-ol-1 (V) and 2,5-dimethylhexen-4-ol-2 (VIII). Distillation at atmospheric pressures with a trace of sulfuric acid results in isomerization to the corresponding tetrahydrofuran derivatives: 2,2-methylethyltetrahydrofuran (III), 2,2-methyl-n-butyltetrahydrofuran (VI), and 2,2,4,4-tetramethyltetrahydrofuran (IX).

In addition, the tetrahydrofuran derivatives (III) and (VI) are obtained on distillation of glycols (I) and (IV) with H_2SO_4 (pH 1.6) together with alcohols (II) and (V), which conclusively shows that unsaturated β-ethylenic alcohols are indeed the primary products of dehydration of the types of γ-glycols of the aliphatic series under investigation.

The structure of alcohol (V), obtained for the first time, and of its corresponding tetrahydrofuran derivative (VI) was proved by oxidation with potassium permanganate; in the first case methylbutyl ketone and acrylic acid were obtained; in the second case γ-methyl-γ-hydroxycaprylolactone:



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EXPERIMENTAL

Synthesis of 2,5-dimethylhexanediol-2,5 (VII). This glycol was prepared by the reaction of ethylmagnesium bromide with the ethyl ester of succinic acid. After decomposition of the organomagnesium complex, extraction, drying, and driving off the ether, crystals of the glycol came down, m.p. 87-88°; the literature data [2] give: m.p. 88.5-89°. The aqueous solution, obtained upon decomposition, was extracted in an extractor. The total yield of the glycol was 34.5%.

Preparation of 2,5-dimethylhexen-4-ol-2 (VIII). 6.6 g of the glycol was placed in a Wurtz flask with a solution of sulfuric acid (pH 1.6). The distillation product immediately decolorized $KMnO_4$ solution. Yield 2.4 g (42%).

B.p. 63.5-64° (15 mm), d_4^{20} 0.8489, n_D^{20} 1.4438, MR_D 40.46; calc. 40.20.

Found %: C 75.05; H 12.60; OH 13.41. $C_8H_{16}O$. Calculated %: C 75.00; H 12.50; OH 13.29.

Literature data [3] give: b.p. 165-166°.

Upon distillation with a drop of concentrated sulfuric acid, the unsaturated alcohol (VIII) converted to tetrahydrofuran (IX). Yield 44%.

B.p. 115.5-116.5°, d_4^{20} 0.8089, n_D^{20} 1.4014, MR_D 38.44; calc. 38.57.

Found %: C 74.83; H 12.76; $C_8H_{16}O$. Calculated %: C 75.00; H 12.50.

Literature data [2] give: b.p. 116-117°, d_4^{20} 0.8113.

Synthesis of 4-methylhexanediol-1,4 (I) was carried out by the reaction of ethylmagnesium bromide with acetopropyl alcohol. After the usual treatment, the compound was vacuum-distilled. Yield 33%.

B.p. 118-119° (8 mm), n_D^{20} 1.4571.

Literature data [4] give: b.p. 139-140° (22 mm), n_D^{20} 1.4575.

The prepared glycol was distilled with sulfuric acid (pH 1.6). After vacuum-distillation of the reaction products, we obtained two fractions:

1st, b.p. 27-28° (14 mm), n_D^{20} 1.4204; 2nd, b.p. 75.5-76° (12 mm), d_4^{20} 0.8617, n_D^{20} 1.4495, MR_D 35.52; calc. 35.58.

Found %: C 73.52; H 12.45; OH 14.88. $C_7H_{14}O$. Calculated %: C 73.68; H 12.28; OH 14.91.

Literature data [4] give: b.p. 169-170°, d_4^{17} 0.8610, n_D^{17} 1.4510.

The 1st fraction corresponded to the oxide III, yield 17%; the 2nd corresponded to alcohol (II), yield 15%. Upon distillation of alcohol (II) with a drop of concentrated sulfuric acid, it converted to tetrahydrofuran (III), yield 65%.

B.p. 121-122°, d_4^{20} 0.8553, n_D^{20} 1.4196, MR_D 33.70; calc. 33.85.

Found %: C 73.56; H 12.39. $C_7H_{14}O$. Calculated %: C 73.68; H 12.28.

Literature data [4] give: b.p. 119-121°, d_4^{20} 0.8593, n_D^{20} 1.4230.

4-Methyloctanediol-1,4 was prepared by reaction of butylmagnesium bromide with acetopropyl alcohol. After decomposition of the organomagnesium complex, extraction, drying and vacuum-distillation, we obtained a 30% yield of glycol, based on the reacted acetopropyl alcohol; 20% was returned.

B.p. 144-145° (15 mm), d_4^{20} 0.9158, n_D^{20} 1.4573, MR_D 46.52; calc. 46.81.

Found %: C 67.62; H 12.47; OH 21.31. $C_9H_{20}O_2$. Calculated %: C 67.50; H 12.50; OH 21.19.

Literature data [5] give: b.p. 119° (3.5 mm), d_4^{20} 0.9389, n_D^{20} 1.4587.

Upon vacuum-distillation of the products obtained upon distillation of glycol (IV) with sulfuric acid (pH 1.6), we separated two fractions: 1st γ-oxide (VI), yield 32.5% and 2nd, alcohol (V), yield 24.58%.

Alcohol (V): b.p. 99.5-100° (17 mm), d_4^{20} 0.8524, n_D^{20} 1.4524, MR_D 44.97; calc. 44.82.

Found %: C 76.19; H 12.75; OH 11.81. $C_9H_{18}O$. Calculated %: C 76.06; H 12.68; OH 11.97.

Oxide (VI): b.p. 55-56° (10 mm), d_4^{20} 0.8507, n_D^{20} 1.4300, MR_D 43.12; calc. 43.09.

Found %: C 76.21; H 12.76. $C_9H_{18}O$. Calculated %: C 76.06; H 12.68.

Literature data [6] give: b.p. 168-169°, d_4^{20} 0.8570, n_D^{20} 1.4298.

Alcohol (V) was distilled at atmospheric pressure with a drop of concentrated sulfuric acid. The boiling point of the prepared oxide (VI) was 164.5-165.5°, n_D^{20} 1.4301.

Oxidation of 2,2-methyl-n-butyltetrahydrofuran (VI). 9.5 g of $KMnO_4$ was needed to oxidize 6 g of tetrahydrofuran. Oxidation was carried out at first with a 1% $KMnO_4$ solution and then the salt was added in the form of a finely ground powder. Oxidation was continued for 7 days. There were no neutral oxidation products. The obtained solution of salts was steamed down, acidified with sulfuric acid and extracted with ether. The product obtained was vacuum-distilled.

B.p. 113-114° (14 mm), equiv. 157.7. $C_9H_{16}O_2$. Calculated equiv. 156.

The lactone (X) obtained, was dissolved in ammonia with heating over a water bath, the excess of ammonia was removed by evaporation and a concentrated solution of the calculated quantity of silver nitrate salt was added to the solution; a snow-white precipitate of the silver salt came down.

Found %: Ag 38.02. $C_9H_{17}O_3Ag$. Calculated %: Ag 38.43.

Oxidation of 4-methylocten-3-ol-1 (V). 22.5 g of $KMnO_4$ was needed to oxidize 6 g of the alcohol. The oxidation was complete after 3 hours. The neutral products were steam-distilled and the distillate was concentrated several times by repeated distillation. The first drops of the last distillate were collected in a solution of 2-4-dinitrophenylhydrazine. The obtained 2,4-dinitrophenylhydrazone of methylbutyl ketone was twice recrystallized from methyl alcohol. M.p. 103-104°.

Literature data [7] give: m.p. 106°.

Found %: N 20.22. $C_{12}H_{16}O_4N_4$. Calculated %: N 20.00.

The obtained solution of salts was evaporated down, acidified with sulfuric acid and extracted with ether. The product obtained was distilled at atmospheric pressure; the fraction that boiled at 144-147° (boiling point of acrylic acid is 144°) was collected.

Found equiv. 73.40. $C_3H_4O_2$. Calculated equiv. 72.06.

A solution of the calculated quantity of $AgNO_3$ was added to the solution of the potassium salt of acrylic acid which was obtained upon titration.

Found %: Ag 60.19. $C_3H_3O_2Ag$. Calculated %: Ag 60.34.

SUMMARY

1. A study was made of the dehydration of 2,5-dimethylhexanediol-2,5; 4-methylhexanediol-1,4 and 4-methyloctanediol-1,4.

2. It was established that in all these cases the primary products of dehydration of the glycols are β-ethylenic alcohols which then isomerize to tetrahydrofuran derivatives.

3. It was established that this mechanism of dehydration is general for primary-tertiary γ-glycols of the aliphatic series.

4. It is also highly probable that this dehydration mechanism is also general for ditertiary γ-glycols of the aliphatic series.

5. The unsaturated alcohol, 4-methylocten-3-ol-1, was prepared for the first time and its structure elucidated.

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THE CHLORINATION OF KETENE

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Although the literature contains some indications [1,2] to the effect that reaction of ketene with chlorine proceeds very smoothly with formation of chloroacetyl chloride as the sole reaction product, these indications are obviously not adequately supported by experiment since nobody has hitherto undertaken a close study of this reaction.

Our preliminary exploratory experiments showed that reaction of ketene with chlorine proceeds at high velocity and is strongly exothermic; we therefore conducted this reaction by mixing 97-98% gaseous ketene with an equimolar amount of chlorine inside a vertical bulb-type water condenser attached to a flask. Reaction was instantaneous when the gases were mixed and the resultant products condensed and ran down into the flask. On distillation, a product boiling at 51-52.5° was collected, which proved to be acetyl chloride, apart from a main fraction with b.p. 103-105° (the boiling point of chloroacetyl chloride is 103-104°). Initially we attributed the formation of acetyl chloride to traces of water which might have been present in the chlorine; we therefore carefully dried the latter, but the amount of acetyl chloride formed was not reduced. It was then decided to make a study of the composition of the main fraction of reaction products which previous investigators had assumed to be pure chloroacetyl chloride. Due to the closeness of the boiling points of the chlorides of mono-, di- and trichloroacetic acids, this study could only be undertaken by analytical methods. Dichloroacetic acid was determined after alkaline hydrolysis in the form of oxalic acid [3]; trichloroacetic acid by decomposition to chloroform and carbon dioxide [4], and chloroacetic acid by difference. The accuracy of this method of analysis, perfected with artificial mixtures, was checked by determination of the total content of chlorine, and also several times by conversion of the mixture of chlorides of chloroacetic acids to their methyl esters which are readily fractionated in a column of medium efficiency (20-30 theoretical plates).

In all these experiments it was found that the fraction of product distilling at 103-105° contained, apart from chloroacetyl chloride, considerable amounts of dichloroacetyl chloride, but no trichloroacetyl chloride. Depending upon the ratio of chlorine to ketene, the amount of dichloroacetyl chloride ranged from 15 to 50%. It is also important to note that the molar amount of acetyl chloride formed during the reaction was always slightly lower than the amount of dichloroacetyl chloride. This indicated partial separation of hydrochloric acid. We subsequently confirmed the formation of the latter directly by a large-scale experiment. In this way we established that chlorination of ketene not only leads to formation of the product of the addition of chlorine – chloroacetyl chloride – but the latter is invariably accompanied by dichloroacetyl chloride. The hydrochloric acid formed in this process in part reacts with ketene to form acetyl chloride.

It was still not clear, however, how dichloroacetyl chloride was formed. At the outset it might be thought that it is the result of subsequent chlorination of the product of primary reaction – chloroacetyl chloride. Accordingly, we tried to minimize the formation of this substance by shortening the period of contact of the reaction product with chlorine by lowering the temperature and diminishing the amount of chlorine to 0.5 mole per mole of ketene. Even under these conditions, however, the reaction product contained not less than 12-15% dichloroacetyl chloride. We thereupon decided to investigate the chlorination of chloroacetyl chloride. It was found that in the absence of catalysts, the reaction does not proceed even with prolonged introduction of chlorine into boiling chloroacetyl chloride. As catalysts we employed phosphorus trichloride, sulfur monochloride, iodine, "triple catalyst" (mixture of iodine, phosphorus pentachloride and red phosphorus), and iron filings. In all the experiments, with fairly prolonged action of chlorine on chloroacetyl chloride both in the cold and with heating, no increase in weight of the reaction mass was observed. Chlorination therefore did not take place. Only when using pyridine as catalyst was a new product, boiling at 106-112°, obtained. Analysis showed it to contain 30% of the original

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chloroacetyl chloride, about 5% dichloroacetyl chloride, and about 65% trichloroacetyl chloride. This clearly demonstrates that in presence of pyridine dichloroacetyl chloride reacts with chlorine with greater facility than does the original chloroacetyl chloride.

As was said above, trichloroacetyl chloride is absent from the products of chlorination of ketene. This circumstance, as also the inability of chloroacetyl chloride to be chlorinated in the absence of a catalyst, leads us to think that in the chlorination of ketene, dichloroacetyl chloride is formed not from chloroacetyl chloride but by another mechanism. It might be thought, however, that when this reaction is carried out in the gas phase a high temperature would be developed at the place of contact of the substances with consequent change of the ratio and reactivity of the products; in later experiments we therefore used an inert solvent (nitrobenzene and pure chloroacetyl chloride) with strict control of the temperature. In these experiments, performed at -18 to +105°, dichloroacetyl chloride was obtained together with chloroacetyl chloride at all the temperatures in this range. The amount of dichloroacetyl chloride in the product ranged from 15 to 50% depending upon the molar ratio of ketene to chlorine taken into reaction. The maximum yield of dichloroacetyl chloride was obtained when this ratio was 1:2, and the lowest yield was obtained when chlorine was passed into excess of ketene dissolved in chloroacetyl chloride. It should be mentioned that in the latter case the total yield of products of the ketene reaction was very small since ketene polymerizes fairly rapidly.

The experiments demonstrate, in our opinion, that under our selected conditions the ketene reacts not by an ionic but by a radical mechanism. Indeed, if the converse were true, hydrochloric acid would have reacted with ketene much more rapidly than chlorine. Formation of dichloroacetyl chloride, again, is not the result of chlorination of chloroacetyl chloride but of some other substance formed (even if only transiently) under conditions of radical attack of ketene by chlorine. This substance might be chloroketene, formation of which was assumed under the reaction conditions. Subsequently chloroketene might react with chlorine and add on two atoms of chlorine at the double ethylenic bond. This side reaction proceeds in parallel with the main reaction of addition of chlorine to the double bond of ketene with formation of chloroacetyl chloride.

EXPERIMENTAL

Preparation of ketene. The ketene necessary for the work, was prepared in a special apparatus by pyrolysis of acetone. The gases from pyrolysis together with acetone passed through a system of condensers in which the main part of the acetone was separated out. Further, the mixture of gases passed into a condenser coil with a temperature of -80° where ketene with the acetone residue was condensed and the uncondensed pyrolysis fumes were discarded. The concentrated (50%) solution of ketene in acetone then flowed evenly into the vaporizer in which the ketene was again evaporated down and separated from the acetone. The resulting ketene was gaseous, 97-98%, with an admixture 1-2% of ethylene.

Reaction of ketene and chlorine in gaseous phase. The apparatus into which the gases were passed was a spherical condenser with an extra sealed-in inner tube. The ketene passed into the condenser along the sealed-in tube and the chlorine passed around it; the gases mixed in one of the bulbs in the cooling zone. The ketene and chlorine were fed in equal streams with the aid of specially graduated rheometers. The chlorine from the cylinder was first dried, passing through two bottles containing sulfuric acid. The liquid which formed in the reaction flowed down along the condenser into the flask. After the experiment, it was fractionated and fractions were collected: 51-52.5° (acetyl chloride), 52.5-104° (intermediate) and 104-106°(main). The main fraction was analyzed for content of chloro-, dichloro- and trichloroacetyl chlorides. The experimental results are given in Table 1.

Besides the experiments given in Table 1, an experiment was undertaken using a 3-fold quantity of chlorine. In order to increase the yield of dichloroacetyl chloride, we performed the experiment without cooling the reaction zone with running water; thereupon, the temperature rose so high that at one time there was an explosion. The total yield of products in this experiment was 32.5 g (from 13.5 g of ketene and 69 g of chlorine), somewhat less than in the other experiments. The dichloroacetyl chloride content of this product was 37%. A final experiment was performed, controlling the temperature in the reaction zone; it was held in the interval 150-200°. For this experiment it was necessary to dilute the chlorine with 3-4 volumes of nitrogen. From 14.2 g of ketene and 29 g of chlorine (ratio 1:1.2), we obtained 40.1 g of product, which contained 24.8% of dichloroacetyl chloride.

Reaction of ketene and chlorine in organic solvents. For solvents we used nitrobenzene and pure chloroacetyl chloride, prepared from chloroacetic acid and thionyl chloride. The experiments were performed in a 4-necked flask, fitted with condenser, stirrer, thermometer and two bubblers. The flask was externally cooled

with ice and salt or dry ice in kerosine. Ketene and chlorine in equimolecular quantities were passed into the cooled solvent with mechanical stirring. When the reaction was complete, the addition in weight of the reaction mass was determined and an analysis was performed for content of dichloroacetyl chloride and distillation. The experimental results are given in Table 2.

TABLE 1

Exp. No.	Quantity of ketene (in g)	Quantity of chlorine (g)	Ratio of ketene to chlorine (moles)	Yield of product (g)	Yield upon distillation of fraction with b.p. (in g)				Analytical results for main fraction (%)	
					51-52.5°	52.5-104°	104-106°	residue	chloroacetyl chloride	dichloroacetyl chloride
1	17.4	29.5	1:1	41.5	6.2	1.5	21.2	10.8	81.8	18.2
2	29.0	59.6	1:1.2	82.6	8.6	4.27	56.5	9.2	73.8	26.2
3	30.0	66.0	1:1.5	86.4	5.45	3.8	60.5	10.0	74.5	25.5
4	23.0	78.0	1:2	68.1	3.03	2.95	40.5	6.8	62.0	38.0

TABLE 2

Exp. No.	Quantity (g)		Solvent		Temperature	Addition in wt. (g)	Content of dichloroacetyl chloride (in %)		Quantity of ketene used (%)
	ketene	chlorine	name	quantity (in g)			total	recalculated on weight addition	
1	24.0	40	Nitrobenzene	117.8	+2°	71.8	18.50	18.5	66
2	20.8	35	Chloroacetyl chloride	88.6	0	66.3	9.25	21.7	72
3	18.5	32	Ditto	80.6	−18	58.1	10.40	24.8	79
4	17.0	29	"	42.0	−18	58.0	15.00	25.8	84
5	13.0	22	"	100.4	−18	51.2	5.04	14.7	−

It must be noted that in Experiment 1 (Table 1), carried out in nitrobenzene, a considerable portion of the product could not be distilled off from the nitrobenzene, and therefore, the following experiments were performed in chloroacetyl chloride.

Experiments 2 and 3 differed only in the temperature of carrying out the reaction. The data of Table 2 show that the content of dichloroacetyl chloride was almost unchanged. In Experiment 4, air was mixed with the chlorine; in Experiment 5, all the ketene was first dissolved in chloroacetyl chloride and chlorine was then passed into this solution. It is evident that in the last case there was the least dichloroacetyl chloride obtained. However, in this case considerably smaller amounts of reaction products were obtained: distillation of the fraction with b.p. 104-105° yielded about 100 g, i.e. almost the same quantity in which the solvent was taken for the reaction. A large amount of solid residue remained in the flask.

Similar experimental results were obtained in those experiments in which additions of dinitrochlorobenzene, trinitrobenzene, chloranil, phosphorus trichloride, etc., were tested for catalysis. These additions did not appreciably affect the ratio in which the chloro- and dichloroacetyl chlorides were formed.

A series of experiments was also carried out in which ketene and chlorine were reacted in boiling chloroacetyl chloride. A description of this enlarged experiment, the conditions of which might serve as a basis for the preparation of mixtures of acid chlorides and chloro- and dichloroacetic acids and individual methyl esters of these acids, is given below.

200 g of a mixture of chloro- and dichloroacetyl chlorides (42.5% dichloroacetyl chloride) was poured into a two-liter round-bottom flask fitted with two bubblers and a spherical reflux water condenser (20 balls) connected to a lowered condenser coil (cooled to −50°) and an even stream of ketene (65 g/hour) and chlorine (220 g/hour)

were passed through the set-up. The reaction mass in the flask started boiling almost immediately due to the heat of reaction and then boiled evenly. The acetyl chloride which formed was almost completely carried out of the flask together with the gaseous hydrogen chloride and condensed in the condenser coil. The liquid of the flask and condenser was periodically combined. The experiment was completed after 14.5 hours. We obtained 2200 g of a mixture of chloro- and dichloroacetyl chlorides, which contained 45.7% dichloroacetyl chloride, and in the distillate there was 267 g of acetyl chloride, which totaled 94%, based on the ketene used.

For conversion to methyl esters 625 g of anhydrous methyl alcohol was slowly poured into the above mixture. The esters were washed with water and after drying with calcium chloride, they were fractionated in a packed column (12 theoretical plates). We obtained 1050 g of the methyl ester of chloroacetic acid, b.p. 128-130°, and 900 g of the methyl ester of dichloroacetic acid, b.p. 140-142°.

Chlorination of chloroacetyl chloride in the presence of pyridine. 38.9 g of chloroacetyl chloride was placed in a 3-necked flask fitted with reflux condenser, bubbler and thermometer, and 1.1 g of pyridine was carefully added; the product was heated to 75-80° and at this temperature chlorine was passed in at the rate of 90 ml/minute. After 3.5 hours, when the addition in weight of the product was equal to 10 g, the passage of chlorine was halted and the product (48.9 g) was distilled; it boiled at 106-112°. The analytical results for the product were: 31% chloroacetyl chloride, 5.2% dichloroacetyl chloride, and 65.4% trichloroacetyl chloride.

SUMMARY

1. Contrary to the literature data, the reaction of ketene with chlorine in the gas phase and in solvents leads, regardless of the ratio of reactants, to formation of a mixture of chloroacetyl and dichloroacetyl chlorides. Acetyl chloride is formed in small amount at the same time.

2. Reaction of ketene with chlorine may serve as a convenientpreparative method for obtaining mixtures of chloro- and dichloroacetic acids.

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SYNTHESIS AND INVESTIGATION OF 1,1-DI-α-NAPHTHYL-2-PHENYL-2-BROMOETHYLENE

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In previous publications [1] we showed that bromination of unsaturated compounds proceeds in various directions depending upon the nature of the radicals and the substituting groups.

Thus, for example, in bromination of α,α-(p-dimethylaminophenyl)-β-phenylethylene, bromine substitutes the hydrogens of the aromatic nuclei, but in the absence of substituents the bromine only replaces the hydrogen of the ethylenic grouping with formation of bromoethylenes, in agreement with the observations of Meisenheimer [2].

Later, we established that the rule is followed when one phenyl is replaced by α- or β-naphthyl, i.e. bromine substitutes the hydrogen of the ethylenic group.

It was of interest to elucidate the mechanism of bromination of olefinic hydrocarbons in presence of two naphthyl radicals at one of the carbons. Apart from its theoretical value, this reaction is of practical importance since we know that some phenylated derivatives of bromoethylene possess estrogenic and anticancerigenic activity, for example, triphenylbromoethylene, diethoxytriphenylbromoethylene, etc. [3].

1,1-Di-α-naphthylphenylethylene is not described in the literature. The problem of the mechanism of its bromination could not therefore be solved before. We were interested, furthermore, in studying the relation between chemical structure and biological action of 1,1-di-α-naphthyl-2-phenyl-2-bromoethylene (III), which could be determined by tests on mice.

It was thought that the synthesis could be most conveniently performed, by analogy with the previous work by reaction of benzyl magnesium chloride with di-α-naphthyl ketone followed by dehydration of the di-α-naphthylbenzylcarbinol (I) and bromination of the resultant 1,1-di-α-naphthyl-2-phenylethylene (II) according to the scheme:

$$\begin{array}{c} C_{10}H_7-COH-C_{10}H_7 \\ | \\ CH_2 \\ | \\ C_6H_5 \\ (I) \end{array} \xrightarrow{-H_2O} \begin{array}{c} C_{10}H_7-C-C_{10}H_7 \\ \| \\ CH \\ | \\ C_6H_5 \\ (II) \end{array} \xrightarrow{+Br_2} \begin{array}{c} C_{10}H_7-C-C_{10}H_7 \\ \| \\ CBr \\ | \\ C_6H_5 \\ (III) \end{array}$$

Apart from this, it was considered of interest to investigate the mechanism of direct bromination of di-α-naphthylbenzylcarbinol (I). It could be imagined that in the absence of substituents in the aromatic rings the hydrogen of the methylene group would first be substituted with formation of hydrobromic acid capable of entering into reaction with the tertiary hydroxyl with formation of 1,1-di-α-naphthyl-2-phenyl-1,2-dibromoethane (IV). Detachment of hydrobromic acid in this system should be expected to lead to 1,1-di-α-naphthyl-2-bromo-2-phenylethylene (III):

$$(I) \xrightarrow{+Br_2} \begin{array}{c} C_{10}H_7-COH-C_{10}H_7 \\ | \\ CHBr \\ | \\ C_6H_5 \end{array} \xrightarrow{HBr} \begin{array}{c} C_{10}H_7-CBr-C_{10}H_7 \\ | \\ CHBr \\ | \\ C_6H_5 \\ (IV) \end{array} \xrightarrow{-HBr} (III)$$

The experiments confirmed the possibility of this mechanism; on bromination of di-α-naphthylbenzylcarbinol, 1,1-di-α-naphthyl-2-phenyl-2-bromoethylene is actually formed.

Dehydration of di-α-naphthylbenzyl carbinol in presence of potassium bisulfate went with perfectly satisfactory yields (84%) but the melting point of the resultant 1,1-di-α-naphthyl-2-phenylethylene proved extremely unsharp; melting started at 72° and was not quite complete at 180°. This may be attributed to the presence of traces of isomeric ketones in the di-α-naphthyl ketone, for example α,β-dinaphthyl or β,β-dinaphthyl ketones. This question was not further studied.

For confirmation of the structure of dinaphthylphenylethylene (II), the latter was oxidized with potassium permanganate to form di-α-naphthyl ketone and benzoic acid. The structure of the bromoethylene derivative was also confirmed by oxidation with permanganate; in this case, apart from di-α-naphthyl ketone and benzoic acid, potassium bromide was detected; the bromine content of the bromo derivative corresponded to 1,1-di-α--naphthyl-2-phenyl-2-bromoethylene.

Pharmacological investigations of 1,1-di-α-naphthyl-2-phenyl-2-bromoethylene, carried out by T.A. Melnikova, showed that this compound possesses estrogenic activity.

EXPERIMENTAL

Synthesis of 1,1-di-α-naphthylbenzylcarbinol. A solution of 25.2 g of benzyl chloride in 75 ml of ether was added with stirring to 4.8 g of magnesium in 50 ml of ether in the presence of several iodine crystals. The reaction was carried out at the boiling point of ether followed by heating for one hour. Then, at 0° a solution of 14.1 g of di-α-naphthyl ketone in 400 ml of ether was added to the reaction mixture. The reaction went vigorously, the mixture turned brown and then light green and yellow and a voluminous crystalline precipitate came down. After addition of the ketone, the reaction mixture was heated for 2 hours on a water bath and was set aside overnight. The product was decomposed with a saturated aqueous solution of ammonium chloride with ice. After separation of the ethereal layer, the aqueous layer was extracted with ether, and the combined ethereal extract was dried over calcined sodium sulfate. After driving off the ether, the residue (38 g) was an almost colorless oily liquid with the odor of dibenzyl and crystallized upon cooling. After separation, washing with alcohol and recrystallization from alcohol, we obtained 4.1 g of colorless prismatic crystals, m.p. 160-162°; we also obtained 1.03 g more from the mother liquor. Yield 26.5% with respect to the di-α-naphthyl ketone.

Found %: C 90.01, 89.55; H 6.10, 5.96; OH 4.47, 4.53; M 369, 377.9. $C_{28}H_{22}O$.
Calculated %: C 89.80; H 5.92; OH 4.47; M 374.5.

On the basis of the experimental data the product melted at 160-162° and corresponded to di-α-naphthylbenzylcarbinol.

It must be noted that during the reaction of benzyl magnesium chloride with di-α-naphthyl ketone, besides di-α-naphthylbenzylcarbinol, benzyl alcohol and dibenzyl are also formed, i.e. hydrolysis of the benzyl magnesium chloride takes place together with coupling of benzyl radicals due, evidently, to reduction reactions. The latter factor affected the yield of tertiary carbinol (did not exceed 26.5%), and only when the organomagnesium synthesis was performed in a stream of nitrogen and when the reaction product (carbinol) was kept in a stream of CO_2, did the yield of carbinol increase to 50%.

After naphthylbenzylcarbinol was removed from the mother liquor, ethyl alcohol was driven off under reduced pressure and 32 g of the oily liquid which remained was distilled twice. We obtained a fraction, b.p. 205-206.5° (762 mm), n_D^{20} 1.5390, which corresponded to benzyl alcohol (literature data [4] give: b.p. 205.5°, n_D^{20} 1.5395) and a fraction that boiled at 108-111° (3 mm) which rapidly crystallized (from alcohol); a test mixture with dibenzyl gave no depression.

In connection with the low yields of 1,1-di-α-naphthylbenzylcarbinol we carried out its synthesis in the same manner as before, but in a nitrogen atmosphere. In this case the yield of di-α-naphthylbenzylcarbinol reached 50%. The side products which we detected were dibenzyl and a resinous residue which was not further investigated (benzyl alcohol was not detected).

Dehydration of di-α-naphthylbenzylcarbinol. 2 g of the compound, dissolved in 25 ml of benzene, was heated for 1 hour on a water bath with 3 g of fused potassium bisulfate. After filtration, driving off the benzene and recrystallization from alcohol, we obtained 1.16 g (84%) of slightly yellowish crystalline substance which began to melt at 72° and converted to a rather cloudy liquid at 180°.

Found %: C 94.09, 94.29; H 5.49, 5.59; M 351.4, 360.2. $C_{28}H_{20}$.
Calculated %: C 94.38; H 5.61; M 356.

0.5 g of the substance was dissolved in 5 ml of ether and was oxidized by being shaken for 6 hours with 400 ml of 2% potassium permanganate solution and 2 g of sodium bicarbonate. The manganese dioxide which separated out was washed with hot water and extracted with hot alcohol. After a large portion of the alcohol had been driven off, crystals separated out which after recrystallization from a mixture of alcohol and ether (1:1), melted at 98-100° and gave no depression in a test mixture with known di-α-naphthyl ketone. After the manganese dioxide was removed, the aqueous filtrate was concentrated and acidified with dilute sulfuric acid; at this point a crystalline substance separated out which melted at 119.5-122° (from hot water) and gave no depression in a test mixture with known benzoic acid. On the basis of the formation of di-α-naphthyl ketone and benzoic acid upon oxidation, the structure of the compound was found to be that of 1,1-di-α-naphthyl-2-phenylethylene.

Bromination of 1,1-di-α-naphthyl-2-phenylethylene. 1.5 g of 1,1-di-α-naphthyl-2-phenylethylene was mixed with 0.5 g of dioxane dibromide, dissolved in 15 ml of ether and washed with a 5% solution of sodium bicarbonate and water. After the ether was driven off under reduced pressure, the residue was a yellow transparent, resinous substance which after 2-fold recrystallization from hot alcohol using activated carbon, melted at 142-144°. We obtained 1.8 g (98%) of light yellow crystals which melted at 149-151° after recrystallization from an alcohol-acetone mixture (1:1).

Found %: Br 18.08, 18.31 (according to Stepanov's method); M 400.6, 412.2. $C_{28}H_{19}Br$.
Calculated %: Br 18.39; M 435.

The analytical data correspond to 1,1-di-α-naphthyl-2-phenyl-2-bromoethylene.

Bromination of di-α-naphthylbenzylcarbinol. 0.5 g of dioxane dibromide was added to 1 g of di-α-naphthylbenzylcarbinol in 10 ml of ether and, after 30 minutes of heating on a water bath, the hydrogen bromide was driven off. The ethereal solution was washed with soda solution, water and dried over calcined sodium sulfate. After the ether was driven off, the yellow, resinous residue was recrystallized from alcohol, activated carbon being used. After recrystallization from an alcohol-acetone (1:1) mixture, the crystalline product melted at 149.5-151° and gave no depression in a test mixture with previously prepared 1,1-di-α-naphthyl-2-phenyl-2--bromoethylene.

Found %: Br 18.10, 18.27 (according to Stepanov's method); $C_{28}H_{18}Br$.
Calculated %: Br 18.39.

SUMMARY

1. The synthesis of di-α-naphthylbenzylcarbinol from benzyl magnesium chloride and di-α-naphthyl ketone was studied; benzyl alcohol and dibenzyl were formed in addition to the carbinol. Performance of the reaction in a nitrogen stream raised the yield of carbinol and suppressed formation of benzyl alcohol.

2. Di-α-naphthylbenzylcarbinol was dehydrated and 1,1-di-α-naphthyl-2-phenylethylene was obtained.

3. It was established that bromine acts upon 1,1-di-α-naphthyl-2-phenyl-ethylene with replacement of the hydrogen of the ethylene group and formation of 1,1-di-α-naphthyl-2-phenyl-2-bromoethylene.

4. It was shown that 1,1-di-α-naphthyl-2-phenyl-2-bromoethylene can also be obtained by direct bromination of di-α-naphthylbenzylcarbinol; the mechanism of the bromination reaction was evaluated.

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INVESTIGATION OF THE ACTION OF BROMINE UPON 1-PHENYL-1-α-(OR β-)-NAPHTHYL-2-METHYLETHYLENES

A.M. Khaletsky and A.Ya. Kaplan

Although numerous papers have been published on the halogenation of substituted ethylenes, it is impossible in a series of cases to predict the mechanism of the reaction. Thus, for example, in the bromination of 1-methyl-1-cyclohexyl-2-phenylethylene, two bromine atoms add on at the double bond [1]; but on bromination of 1,1-bis-4,4-dimethylaminophenyl-2-phenylethylene, bromine does not add on, bromine substitution taking place at the hydrogens of the aromatic nuclei containing the substituents [2]. In the latter case an important part is undoubtedly played by electronegative groups capable of displacement of electrons and stabilization of hydrogen at the ethylenic bond. This interpretation is supported by the fact that triphenylbromoethylene is readily formed when bromine acts upon diphenylbenzyl carbinol [3].

The biological action (upon mice) of bromoethylenes varies considerably with the position of the halogen; whereas triphenylbromoethylene manifests estrogenic activity in doses of 20 γ, p-bromophenyldiphenylethylene is completely inactive even in doses of over 5000 γ. The cause of the wide variation in biological activity is unknown, but it must be associated with the chemical structure and the position of the halogen, since the estrogenic activity of triphenylbromoethylene drops 50 times when only one hydrogen of the aromatic nucleus is substituted by bromine [4].

The biological activity of bromoethylenes containing naphthyl radicals has not previously been studied. With this objective, we synthesized several of their derivatives, including 1-phenyl-1-α-naphthyl- and 1-phenyl-1-β-naphthyl-2-methyl-2-bromoethylenes. The bromoethylenes were synthesized from 1-phenyl-1-α-(or β-)naphthyl-2-methylethylenes; the latter were obtained by dehydration of the corresponding carbinols – 1-phenyl-1-α-(or β-)-naphthylpropanols-1. Concerning the initial isomeric carbinols, these were likewise prepared by us for the first time by the action of ethyl magnesium bromide on phenyl-α-(or β-)naphthyl ketones. The properties of the carbinols are characteristic: viscous liquids which crystallize with difficulty. Thus, for example, 1-phenyl-1-α-naphthylpropanol-1 crystallized only after 2 years, while its β-isomer has remained liquid to this day.

Dehydration of 1-phenyl-1-α-naphthylpropanol-1 in presence of potassium bisulfate gave 1-phenyl-1-α-naphthyl-2-methylethylene, m.p. 69-71°. For confirmation of the structure it was oxidized with lead tetraacetate in a medium of glacial acetic acid; among the volatile products was detected acetaldehyde in the form of its 2,4-dinitrophenylhydrazone with m.p. 147°. After the acetaldehyde had been distilled off, phenyl-α-naphthyl ketone was detected in the residue, likewise in the form of its 2,4-dinitrophenylhydrazone with m.p. 118-121°; it did not give a depression of melting point with an authentic specimen. The phenyl-α-naphthyl ketone resulting from the oxidation of phenyl-α-naphthyl ketone later crystallized. From the study of the products of oxidation we can conclude that dehydration of phenyl-α-naphthylpropanol-1 gives phenyl-α-naphthyl-2-methylethylene (I).

Bromination of (I) with the help of dioxane dibromide gave a substance with m.p. 92-94° whose bromine content and molecular weight corresponded to 1-phenyl-2-α-naphthyl-2-methyl-2-bromoethylene (II). For confirmation of the structure and, in particular, of the position of the bromine, the product was oxidized with potassium permanganate; acetaldehyde was identified in the form of its 2,4-dinitrophenylhydrazone; phenyl-α-naphthyl ketone and potassium bromide were also found:

$$\begin{matrix} C_6H_5 \\ \alpha\text{-}C_{10}H_7 \end{matrix}\!\!> CHOH - CH_2 - CH_3 \rightarrow \underset{(I)}{\begin{matrix} C_6H_5 \\ \alpha\text{-}C_{10}H_7 \end{matrix}\!\!> C = CH - CH_3} \rightarrow \underset{(II)}{\begin{matrix} C_6H_5 \\ \alpha\text{-}C_{10}H_7 \end{matrix}\!\!> C = CBr - CH_3}.$$

The isomeric 1-phenyl-1-β-naphthylpropanol-1 was synthesized, as mentioned above, from phenyl-β-naphthyl ketone and ethyl magnesium bromide. Dehydration of the carbinol in presence of potassium bisulfate gave a hydrocarbon with m.p. 106.5-107° which on oxidation yielded acetaldehyde (as the 2,4-dinitrophenylhydrazone) and phenyl-β-naphthyl ketone with m.p. 81-82°. On the basis of the data obtained, the hydrocarbon corresponds to the structure of 1-phenyl-1-β-naphthyl-2-methylethylene (Ia). Bromination of the latter with dibromopyridine in a medium of glacial acetic acid gave a substance whose bromine content and molecular weight corresponded to the formula $C_{19}H_{16}Br_2$; oxidation with potassium permanganate gave phenyl-β-naphthyl ketone, potassium bromide and acetaldehyde (as the 2,4-dinitrophenylhydrazone). The data indicate that the dibromide has the structure of 1,2-dibromo-1-phenyl-1-β-naphthylpropane (III):

$$\underset{\text{(Ia)}}{\begin{matrix}C_6H_5\\ \beta\text{-}C_{10}H_7\end{matrix}\!\!>C=CH-CH_3} \rightarrow \underset{\text{(III)}}{\begin{matrix}C_6H_5\\ \beta\text{-}C_{10}H_7\end{matrix}\!\!>CBr-CHBr-CH_3.}$$

Bromination of 1-phenyl-1-β-naphthylpropanol-1 with dioxane dibromide in a medium of glacial acetic acid likewise gave a dibromide $C_{19}H_{16}Br_2$ identical with that previously obtained from 1-phenyl-1-β-naphthyl-2-methylethylene; the following mechanism is therefore proposed:

$$\begin{matrix}C_6H_5\\ \beta\text{-}C_{10}H_7\end{matrix}\!\!>\overset{OH}{\overset{|}{C}}-CH_2-CH_3 \xrightarrow{Br_2} \begin{matrix}C_6H_5\\ \beta\text{-}C_{10}H_7\end{matrix}\!\!>\overset{OH}{\overset{|}{C}}-CHBr-CH_3 \xrightarrow{HBr} \begin{matrix}C_6H_5\\ \beta\text{-}C_{10}H_7\end{matrix}\!\!>CBr-CHBr-CH_3.$$

Pharmacological tests on mice of 1-phenyl-1-α-naphthyl-2-bromo-2-methylethylene and 1,2-dibromo-1-phenyl-1-β-naphthylpropane showed that whereas the monobromo compound possesses estrogenic activity, the dibromo derivative of 1-phenyl-1-β-naphthylpropane has a very low activity. This observation once again emphasizes the importance of the bromine at the double bond for the synthesis of estrogens.

We take this opportunity of thanking T.A. Melnikova for carrying out the biological experiments.

EXPERIMENTAL

1. Preparation of 1-phenyl-1-α-naphthylpropanol-1. At 0° a solution of 25 g of phenyl-α-naphthyl ketone in 75 ml of ether was added to the ethyl magnesium bromide that was prepared from 7.2 g of magnesium and 32.4 g of ethyl bromide in 150 ml of ether. After the ketone was added, the reaction mixture was heated with stirring for 1 hour to the boiling point of ether. In order to decompose the organomagnesium complex, the latter was gradually added to an aqueous solution of ammonium chloride with ice, and gases evolved which were not investigated further (evidently, butane). After the ethereal layer was separated, the aqueous layer was extracted three times with ether and the combined ethereal extracts were washed with water. The ether was driven off. We obtained 29.1 g of a light yellow, transparent, strongly light-refractive, viscous liquid which distilled at 162-186° (1 mm) and which upon reaction with concentrated sulfuric acid turned a violet color which disappeared upon dilution with water. The residue was a dark brown resin which congealed upon cooling. Upon a repeated distillation, the liquid fraction boiled at 162-186° (1 mm), d_{20}^{20} 1.1255, n_D^{20} 1.6139.

Found %: C 86.61, 86.88; H 6.83, 6.87; OH (according to Chugaev-Tserivitinov) 5.86, 6.02; M 273.5.
$C_{19}H_{18}O$. Calculated %: C 87.02; H 6.87; OH 6.48. M 262.37.

After separation of the 1-phenyl-1-α-naphthylpropanol-1, the residue was a dark brown transparent solid mass, easily rubbed to powder and readily soluble in ether, benzene, acetone and hot alcohol. Upon cooling the alcoholic solution, bright orange flakes separated out which, upon being washed with alcohol and dried in a vacuum-desiccator, melted at 67-88°. Attempts to purify the substance by multiple-recrystallizations from alcohol using activated carbon did not change the melting point; with concentrated sulfuric acid the compound turned cherry-red.

Found: M 353.3, 376.2. $C_{38}H_{32}$. Calculated: M 488.

It is possible that the product was the partially impure dimer of 1-phenyl-1-α-naphthyl-2-methylethylene, molecular weight 488.

2. 1-Phenyl-1-α-naphthyl-2-methylethylene (I). 20 g of phenyl-α-naphthylethylcarbinol was heated with 20 g of fused potassium bisulfate and 100 ml of benzene for 2.5 hours at the boiling point of the latter. After separation from potassium bisulfate and elimination of benzene, the filtrate was distilled at 141-151° (2 mm); we obtained 12.8 g of substance and about 7 g of residue. After a second distillation, the fraction (141-151°, 2 mm) boiled at 144-151° (2 mm); it was an almost colorless oily liquid which gave a blood-red coloration with sulfuric acid. When mixed with an equal volume of alcohol or petroleum ether, fine white crystals separated out which after 2 recrystallizations from 80% alcohol in the presence of activated carbon, melted at 72-73° and were lustrous tetragonal prisms. Yield 6.88 g (37%).

Found %: C 93.82, 93.71; H 6.90, 6.82; M 257.09, 238.22.
$C_{19}H_{16}$. Calculated %: C 93.47; H 6.56; M 244.32.

After separation of 1-phenyl-1-α-naphthyl-2-methylethylene, the residue was a solid, transparent, dark-brown mass which was readily rubbed into powder. It was soluble in acetone, benzene, chloroform, petroleum and ethyl ethers and also in hot alcohol. Upon cooling the alcoholic solution, an orange, flaky precipitate separated out which melted at 67-88°. When it was mixed with an equal amount of the residue obtained after separation of 1-phenyl-1-α-naphthylpropanol-1, it gave no melting point depression (67-88°); with concentrated sulfuric acid it gave a cherry-red coloration. Evidently, these residues were identical and were dimers of 1-phenyl-1-α-naphthyl-2-methylethylene.

Oxidation of 1-phenyl-1-α-naphthyl-2-methylethylene. A mixture of 4.2 g of the substance, 10 ml of glacial acetic acid and 5 g of lead tetraacetate was heated to 60° until complete solution and then a 30% potash solution was added to this solution. The gas which evolved was passed into a solution of 2,4-dinitrophenylhydrazine to bind the acetaldehyde. After neutralization, the contents of the flask were extracted with benzene, the benzene extract was washed with water and dried over calcined sodium sulfate. After the benzene was driven off, 2 drops of concentrated sulfuric acid was added to the residue so that in case of formation of phenyl-α-naphthylpropylene glycol, the latter would be dehydrated to the oxide of phenyl-α-naphthylmethylethylene which isomerizes to methylphenyl-α-naphthylacetic aldehyde by the reaction:

$$\begin{matrix}C_6H_5\\ \alpha\text{-}C_{10}H_7\end{matrix}\!\!>C=CH-CH_3 \xrightarrow{(CH_3COO)_4Pb} \begin{matrix}C_6H_5\\ \alpha\text{-}C_{10}H_7\end{matrix}\!\!>\overset{OH}{\overset{|}{C}}-CHOH-CH_3 \xrightarrow[-H_2O]{KHSO_4} \begin{matrix}C_6H_5\\ \alpha\text{-}C_{10}H_7\end{matrix}\!\!>\underset{O}{C-CH}-CH_3 \rightarrow \begin{matrix}C_6H_5\\ \alpha\text{-}C_{10}H_7\end{matrix}\!\!>\overset{CH_3}{\overset{|}{C}}-C\begin{matrix}\!\!{}^{\nearrow O}\\ \!\!{}_{\searrow H}\end{matrix}$$

However, after addition of sulfuric acid, there was an odor of acetic acid and after neutralization of the solution with soda, with ferric chloride it turned red, indicating the presence of acetate-ion. Thus, the oxidation product of phenyl-α-naphthyl-2-methylethylene was not glycol, but evidently the diacetate of 1-phenyl-1-α-naphthyl-2-methylethylene glycol. 4.2 g of the latter was boiled with 25 ml of 1 N alcoholic KOH solution for 30 minutes and after cooling, the unreacted alkali was titrated with 0.1 N HCl solution in the presence of phenolphthalein; 0.7 ml of HCl was consumed which corresponded to the theoretically calculated amount for the diacetate of 1-phenyl-1-α-naphthyl-2-methylethylene glycol.

After filtration, the hydrolysis product was boiled with activated carbon. After the alcohol was driven off in vacuum, however, the filtrate did not crystallize and, therefore, 2.5 g of its residue mixed with 20 ml of glacial acetic acid was oxidized with 5 g of lead tetraacetate in the same manner as previously; the carbon dioxide which evolved displaced the acetaldehyde which was passed into a solution of 2,4-dinitrophenylhydrazine. The yellow precipitate that formed was recrystallized from alcohol and melted at 147°, not giving a depression in mixture with known 2,4-dinitrophenylhydrazone of acetaldehyde.

After the acetic acid was neutralized with potash, the contents of the flask were extracted with ether. After washing with water, drying over calcined sodium sulfate and driving off the ether, the residue was a thick, oily liquid which after being boiled with alcohol, did not yield phenyl-α-naphthyl ketone, but upon addition of an alcoholic solution of 2,4-dinitrophenylhydrazine, it yielded a yellowish-red crystalline precipitate which after recrystallization from alcohol, melted at 118-121°. A test mixture with the known 2,4-dinitrophenylhydrazone of phenyl-α-naphthyl ketone (m.p. 121-122°) gave no depression. It must be noted that in parallel experiments, after two weeks, the alcoholic solution yielded crystals which after recrystallization from alcohol, melted at 73-75° and gave no depression in a test mixture with known phenyl-α-naphthyl ketone, i.e. the direct formation of the latter upon oxidation of the hydrocarbon was shown.

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3. 1-Phenyl-1-α-naphthyl-2-methyl-2-bromoethylene (II). 6.3 g of dioxane dibromide was added with continuous stirring to 5.9 g of phenyl-α-naphthyl-2-methylethylene. The initial decolorization gradually halted and hydrogen bromide was evolved. The reaction mixture was heated for 15 minutes at 75-80°, treated with 5% sodium bicarbonate solution and washed with water until it gave a neutral reaction, extracted with ether and dried over calcined sodium sulfate. After removal of the ether, the compound was distilled at 240-252° (10 mm); it was a viscous, oily liquid which crystallized after 3 days. Upon contact with concentrated sulfuric acid it gave a blood-red coloration. After washing with petroleum ether and recrystallization from 80% alcohol, we obtained 5.8 g of substance which crystallized in the form of lustrous needlelike crystals, m.p. 92-94°.

Found %: Br (according to Stepanov) 24.20; M 303.2, 323.22.
$C_{19}H_{15}Br$. Calculated %: Br 24.72; M 323.22.

Oxidation of 1-phenyl-1-α-naphthyl-2-methyl-2-bromoethylene. A mixture of 4.85 g of the compound, 10 ml of ethyl ether, 316 ml of 1% potassium permanganate solution and 2 g of soda was shaken for 6 hours and the reaction mixture was then set aside overnight. The colorless solution was separated from the manganese dioxide and after washing with hot water and drying, the manganese dioxide was extracted with hot alcohol. Upon cooling the alcoholic solution, a white precipitate separated out which melted at 73-74.5° after recrystallization from alcohol and gave no melting point depression in a test mixture with phenyl-α-naphthyl ketone. After separation from the manganese dioxide, the aqueous filtrate was concentrated to low bulk, neutralized with nitric acid (in the presence of phenolphthalein) and after being boiled, was filtered into a 100 ml volumetric flask. After dilution to the mark in aliquot parts of the given solution, the potassium bromide was determined (according to Volhard), and the potassium acetate was titrated with 0.05 N hydrochloric acid solution in the presence of methyl orange.

Found g: CH_3COOK 0.1450; KBr 0.5865.
Calculated g: CH_3COOK 0.1471; KBr 0.5871.

4. Preparation of 1-phenyl-1-β-naphthylpropanol-1. At −12°, a solution of 15 g of phenyl-β-naphthyl ketone in 75 ml of ether was added in the course of 3 hours to the ethylmagnesium bromide prepared from 4.8 g of manganese filings and 21.6 g of ethyl bromide in 75 ml of ether and the reaction mixture was then heated for 2 hours on a water bath and set aside overnight. Upon decomposition with a saturated aqueous solution of ammonium chloride with ice, gaseous products evolved. After separation of the ethereal layer and treatment as described for the synthesis of 1-phenyl-1-α-naphthylpropanol-1, we obtained about 40 g of thick yellow oily liquid which decomposed at 213° (2 mm). Only after 2 years of standing did the liquid crystallize and upon recrystallization from alcohol, it melted at 115-116°. The product was soluble in benzene, acetone, petroleum ether, difficultly soluble in alcohol in the cold and more readily soluble with heating.

Found %: C 86.64, 86.91; H 6.84, 6.87; OH (according to Chugaev-Tserivitinov) 6.41, 6.30. M 275.1, 271.0.
$C_{19}H_{18}O$. Calculated %: C 87.02 H 6.8; OH 6.48; M 262.37.

5. 1-Phenyl-1-β-naphthyl-2-methylethylene (Ia). 13 g of 1-phenyl-1-β-naphthylpropanol-1 was heated for 1 hour with 6.5 g of fused potassium bisulfate; at 110-120° water separated out. When heating was completed, the substance was dissolved in petroleum ether, the solution was filtered off and after a portion of the solvent had been driven off, crystallization took place. After two recrystallizations from an alcohol-acetone mixture (3:1), we isolated 4.8 g of substance, m.p. 106.5-107°.

Found %: C 93.57, 93.40; H 6.81, 6.56; M 260.00, 258.66.
$C_{19}H_{16}$. Calculated %: C 93.47; H 6.56; M 244.32.

Oxidation of 1-phenyl-1-β-naphthyl-2-methylethylene. A mixture of 2 g of the compound dissolved in 10 ml of glacial acetic acid and 3 g of lead tetraacetate was heated to 60° and further treatment of this mixture was conducted as described for oxidation of 1-phenyl-1-α-naphthyl-2-methylethylene. Final treatment was also the same as in the previous case, i.e. 1.5 g of 1-phenyl-1-β-naphthyl-2-methylethylene glycol (supposed) in 10 ml of glacial acetic acid was oxidized with an additional 2 g of lead tetraacetate and the acetaldehyde which came off was passed into an alcoholic solution of 2,4-dinitrophenylhydrazine. After recrystallization from alcohol, the yellow precipitate that formed melted at 147-147.5° and gave no depression in a test mixture with

the 2,4-dinitrophenylhydrazone of acetaldehyde. After the acetaldehyde was driven off and after neutralization of the acetic acid with potash, the residue was extracted with ether and after being washed with water, it was dried over calcined sodium sulfate and upon distilling off the ether, it solidified. After recrystallization from alcohol, it melted at 81-82°, and gave no depression in a test mixture with known phenyl-β-naphthyl ketone.

Bromination of 1-phenyl-1-β-naphthyl-2-methylethylene. 1.5 g of the compound was dissolved in 10 ml of glacial acetic acid, mixed with a solution of 1.35 g of pyridine dibromide in 5 ml of glacial acetic acid and then heated over a water bath with continuous stirring. After the mixture was decolorized and poured into water, a yellowish flaky precipitate separated out which after being washed with a solution of soda and water, was dissolved in ether and dried over calcined sodium sulfate. After filtration and evaporation of the ether, we obtained a yellowish, resinous substance which did not crystallize from organic solvents.

Found %: Br (according to Rosenmund-Kunganer) 39.06, 38.44; M 402.01, 396.21.
$C_{19}H_{16}Br_2$. Calculated %: Br 39.10; M 404.15.

Bromination of 1-phenyl-β-naphthylpropanol-1. A solution of 2 g of 1-phenyl-1-β-naphthylpropanol-1 in 12 ml of glacial acetic acid was gradually mixed with 2 g of dioxane dibromide. After decolorization ceased, a yellowish crystalline precipitate formed which, after filtration and washing with glacial acetic acid, was converted to a thick viscous mass which was unaltered upon boiling with alcohol.

Found %: Br 38.54.
$C_{19}H_{16}Br_2$. Calculated %: Br 39.10.

SUMMARY

1. The isomeric 1-phenyl-1-α-(and β-)naphthylpropanols-1 were synthesized by the Grignard reaction.

2. Dehydration of 1-phenyl-α-(and β-)naphthylpropanols-1 gave the corresponding isomeric unsaturated hydrocarbons, whose structure was confirmed by oxidation.

3. Bromination of the isomeric 1-phenyl-1-α-(and β-)naphthyl-2-methylethylenes was investigated; it was found that when an α-naphthyl radical is present in the hydrocarbon, the bromine replaces the hydrogen at the double bond; in presence of a β-naphthyl radical, bromine adds on at the double bond.

4. Direct bromination of 1-phenyl-1-β-naphthylpropanol-1 was investigated; a substance $C_{19}H_{16}Br_2$ was obtained which was evidently 2,3-dibromo-3-phenyl-3-β-naphthylpropane.

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SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

XXXIV. 9-METHYL-1,6-DIKETO-Δ^5-OCTAHYDRONAPHTHALENE

I. N. Nazarov, S. I. Zavyalov, M. S. Burmistrova, I. A. Gurvich and L. I. Shmonina

Ketones containing a hydrogenated naphthalene skeleton are important intermediates in the synthesis of steroids and related compounds. Of special interest among these ketones is 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (IV), prepared some years ago in our laboratory by the following scheme [1]:

By a detailed study of these reactions we succeeded in considerably improving the individual steps of this synthesis and in raising the yield of diketone (IV) to 30%, based on the original dihydroresorcinol [1].

Methylation of dihydroresorcinol was performed in various solvents using different metallic derivatives of dihydroresorcinol while varying the temperature and duration of reaction as well as the ratio of reactants. The best results were obtained by methylation of dihydroresorcinol in aqueous acetone solutions in presence of potassium carbonate or sodium carbonate. An examination of the reaction products revealed that, like dimedon, dihydroresorcinol is non-selectively methylated, and dimethyldihydroresorcinol is formed together with methyldihydroresorcinol, while part of the original dihydroresorcinol remains unchanged. By using 0.75 equivalent of potassium carbonate and repeatedly methylating the unreacted dihydroresorcinol, the yield of pure methyldihydroresorcinol was brought to about 50%.

Condensation of methyldihydroresorcinol with methyl vinyl ketone proceeded nearly quantitatively in boiling methanol in presence of 0.05 equiv. potassium hydroxide. Because of its instability, the prepared triketone (III) was used in the next step without distillation.

Methyl vinyl ketone was prepared in 90% yield by hydration of vinylacetylene in aqueous methanol in presence of mercuric sulfate and subsequent cleavage of methanol from methoxybutanone according to the scheme:

$$CH\equiv C-CH=CH_2 \xrightarrow[HgSO_4]{CH_3OH,H_2O} CH_3COCH_2CH_2OCH_3 \xrightarrow{-CH_3OH} CH_3COCH=CH_2$$

For the purpose of cyclization of triketone (III) to 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (IV), various catalysts were used: piperidine salts of butyric, caproic and phosphoric acids, diethylamine phosphate, and ammonium acetate. The best results were obtained on heating triketone (III) with the piperidine salt of phosphoric acid in vacuum at 92-98° for 3 hours; in this manner a 62% yield of diketone (IV) was attained, based on the methyldihydroresorcinol. Diketone (IV) was hydrogenated in solutions of ether, methanol, and

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alcohol over platinum and palladium catalysts, and also in an acid medium. In all cases the main product of reaction was cis-9-methyl-1,6-diketodecalin (V):

(IV) (V)

Heating of diketone (IV) with a mixture of acetic anhydride and acetyl chloride or with ethyl orthoformate in presence of concentrated sulfuric acid led to the unstable enolic ethers (VI) and (VII), which could not be isolated, in analytically pure form. In this connection it should be noted that 6-keto-Δ^5-octahydronaphthalene (VIII) also forms an unstable enolic ether (IX), readily oxidizing in the air [2]:

(VIII) (IX)

EXPERIMENTAL

Methylation of dihydroresorcinol (I). A mixture of 56 g of dihydroresorcinol (I) (m.p. 103-104°), 34.5 g, (equivalent) of potash, 150 ml of water, 300 ml of acetone and 45 ml of methyl iodide was stirred at 60° for 4 hours. After the acetone was driven off in vacuum, a white crystalline precipitate came down which was washed with water and dried. We obtained 26.6 g (42%) of methyldihydroresorcinol (II), m.p. 209-210°.

The mother liquors which remained after methylation of 461 g of dihydroresorcinol were combined and extracted with ether and chloroform. After drying and driving off the solvents, we obtained 166.4 g of oil which upon freezing and crystallization yielded 62.5 g of initial dihydroresorcinol. When the remaining oil was vacuum-distilled, we obtained 81 g of dimethyldihydroresorcinol, b.p. 100-102° (11 mm), m.p. 39-40°. A test mixture with previously [3] prepared dimethyldihydroresorcinol gave no depression.

A mixture of 56 g of dihydroresorcinol, 145 ml of water, 300 ml of acetone, 25.8 g (0.75 equiv.) of potash and 34 ml of methyl iodide was heated for 5 hours at 60°. After the acetone was driven off in vacuum, we isolated 22.4 g of methyldihydroresorcinol. 150 ml of acetone, 11.2 g of potash and 15 ml of methyl iodide were added to the mother liquor. After heating for 3 hours and driving off the acetone in vacuum, we obtained an additional 10.2 g of methyldihydroresorcinol. 120 ml of acetone, 4.6 g of potash and 6.5 g of methyl iodide were added to the remaining mother liquor. After heating for 4 hours and driving off the acetone in vacuum, we obtained 3.2 g more of methyldihydroresorcinol. The total yield of pure methyldihydroresorcinol, m.p. 209-210° was 31 g (50%).

Preparation of methyl vinyl ketone. In the course of 4 hours with stirring, 470 g of vinylacetylene was passed into a mixture (heated to the boil) of 20 g of mercury sulfate, 50 ml of water and 700 ml of methanol at such a rate that the temperature of the solution stayed in the range 60-65°, and simultaneously, 150 ml of water was added drop-wise to the solution. The mixture was stirred for 2 hours at room temperature and on the following day it was neutralized with soda (20 g) using litmus as the indicator, filtered, and distilled once under a slight vacuum (100-200 mm), and then a second time at atmospheric pressure. We obtained 865 g (93.8%) of methoxybutanone, b.p. 136-137°; n_D^{20} 1.4036.

A mixture of 145 g of methoxybutanone and 0.8 g of p-toluenesulfonic acid was heated in a distilling flask fitted with a Vigreux column at 112-116° for 2 hours. 160 ml of distillate was collected which contained 97 g of methylvinyl ketone (semicarbazone, m.p. 141-141.5°).

Condensation of methyl vinyl ketone with methyldihydroresorcinol. 160 ml of the above-described distillate containing 97 g of methyl vinyl ketone was added to a mixture of 103 g of methyldihydroresorcinol and a solution

of 2 g of caustic potash in 60 ml of methanol. The mixture was boiled for 6 hours with stirring and then set aside overnight at room temperature. The following day the methanol was driven off under a slight vacuum (temperature of bath 45°). 60 ml of water was added to the residue and the product was extracted with ether. We obtained 133 g of crude triketone (III) (n_D^{20} 1.4898) which was used without further purification for the preparation of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (IV).

Preparation of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (IV). A mixture of 133 g of the above-described crude triketone (III) (n_D^{20} 1.4898) and 10 g of piperidine salt of phosphoric acid (1 g of phosphoric acid, specific gravity 1.8, to 2.5 g of piperidine) was heated in vacuum (26 mm) at 92-98° for 3 hours. Upon cooling, the resulting mixture (n_D^{20} 1.5290) was shaken with 175 ml of water and 100 ml of benzene. After washing with bicarbonate solution, from the benzene solution we obtained 110 g of oil, n_D^{20} 1.5290, which, after standing, yielded 40 g of 9-methyl-1,6-diketo-Δ^5-octalin (IV), m.p. 45-46°. When the mother liquor (68 g, n_D^{20} 1.5160) was treated a second time with piperidine salt of phosphoric acid (5 g) as described above and then distilled in vacuum (2 mm), we obtained 52.3 g more diketooctalin (IV), m.p. 45-46°. The total yield of diketooctalin 92.3 g (62.5%).

After two recrystallizations from ethyl acetate, the mono-2,4-dinitrophenylhydrazone had m.p. 185.5-186°, $\lambda_{max.}$ 382 mμ (in methanol).

Found %: N 16.13, 16.21. $C_{17}H_{18}O_5N_4$. Calculated %: N 15.63.

The bis-2,4-dinitrophenylhydrazone, prepared from 150 mg of octalin (IV) and 350 mg of 2,4-dinitrophenylhydrazine after being boiled with a mixture of alcohol and ethyl acetate, had m.p. 238-239°, $\lambda_{max.}$ 387 mμ (in methanol).

Found %: N 20.69, 20.84. $C_{23}H_{22}O_8N_8$. Calculated %: N 20.81.

The literature data give m.p. 247-248° [4].

Hydrogenation of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (IV). 1) 0.15 g of diketooctalin was hydrogenated in 5 ml of methanol in the presence of palladium supported on calcium carbonate. In the course of 10 minutes, 23 ml of hydrogen (16°, 746 mm) was absorbed and hydrogenation ceased. After the solvent was driven off and the residue was recrystallized from a mixture of ether and petroleum ether, we isolated 0.1 g of cis-9-methyl-1,6-diketodecalin (V), m.p. 61-63°, which gave no depression with the known compound, prepared by hydrolysis of 9-methyl-6-methoxy-1-keto-Δ^5-octalin [5].

After boiling with a mixture of ethyl acetate and alcohol, the bis-2,4-dinitrophenylhydrazone had m.p. 230.5-231.5°.

Found %: N 20.56, 20.74. $C_{23}H_{24}O_8N_8$. Calculated %: N 20.74.

2) 0.15 g of diketooctalin (IV) was hydrogenated in the presence of palladium supported on charcoal in 5 ml of methanol with the addition of one drop of concentrated hydrochloric acid. 20 ml of hydrogen was absorbed after 45 minutes (18°, 740 mm) and hydrogenation ceased. After the solvent was driven off and the product was recrystallized from n-hexane, we obtained 85 mg of diketodecalin (V).

3) 0.15 g of diketooctalin (IV) was hydrogenated in the presence of palladium supported on calcium carbonate in 6 ml of absolute ether. After 25 minutes, 18 ml of hydrogen (17°, 740 mm) had been absorbed and hydrogenation ceased. We obtained 100 g of diketodecalin (V).

4) 0.15 g of diketooctalin (IV) was hydrogenated in presence of a Pt catalyst in 5 ml of methanol. After 45 minutes, 20 ml of hydrogen (18°, 740 mm) had been absorbed and hydrogenation ceased. We obtained 60 mg of diketodecalin (V). Similar results were obtained for hydrogenation in ethyl alcohol.

5) 0.15 g of diketooctalin (IV) was hydrogenated in 5 ml of methanol in the presence of a Pt catalyst with the addition of 1 drop of concentrated hydrochloric acid. After 15 minutes, 22 ml of hydrogen (18°, 740 mm) was absorbed. We obtained 57 g of diketodecalin (V).

Preparation of enolic acetate of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (VI). A mixture of 2 g of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (IV), 30 ml of acetic anhydride and 50 ml of acetyl chloride was heated in an ampoule at 115-125° for 5 hours. After the volatile fractions were driven off, the residue was vacuum-distilled. We obtained 1.6 g of enolic acetate (VI), boiling range 115-118° (0.05 mm); n_D^{20} 1.5268.

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Found %: C 70.05, 69.55; H 7.25, 7.26. $C_{13}H_{16}O_3$. Calculated %: C 72.5; H 6.9.

Upon standing in the open, the percentage of this hydrocarbon present was greatly reduced.

Preparation of the enolic ether of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (VII). 2 ml of orthoformic ester and 2 drops of concentrated sulfuric acid in 2 ml of dioxane were added to 2 g of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene (IV) in 8 ml of anhydrous dioxane. The mixture was heated for 40 minutes at 100° and upon cooling, was treated with several drops of pyridine; after the solvent was driven off, the residue was vacuum-distilled. We obtained 0.6 g of enolic ether (VII), boiling range 136-140° (4 mm), n_D^{20} 1.5280.

Found %: C 72.87, 72.49; H 8.44, 8.28. $C_{13}H_{18}O_2$. Calculated %: C 75.7; H 8.7.

Upon shaking in the cold with a 1% hydrochloric acid solution, the enolic ether (VII) formed the initial diketone (IV).

SUMMARY

1. A preparative method was developed for the synthesis of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene in 3 steps, starting from dihydroresorcinol. The total yield was 30%.

2. It was shown that catalytic hydrogenation of 9-methyl-1,6-diketo-Δ^5-octahydronaphthalene gives cis-9-methyl-1,6-diketodecalin.

3. It was established that the low yield of methyldihydroresorcinol is due to the non-selectivity of the methylation of dihydroresorcinol.

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β-(PYRIDYL-4)-GLUTARIC ACID AND THE PRODUCTS OF ITS TRANSFORMATIONS

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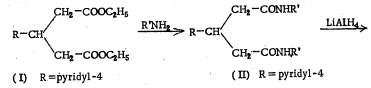
The diethyl ester of β-(pyridyl-4)-glutaric acid (I), described by us in the preceding communication [1], may serve as the starting point for synthesis of compounds of various structures. With amines, (I) reacts to form the corresponding diamides (II), which are reduced by lithium aluminum hydride to derivatives of 3-(pyridyl-4')-diaminopentane (III):



(I) R = pyridyl-4

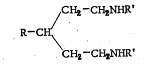
(Ia) R = piperidyl-4

(II) R = pyridyl-4

R' = NH_2, H, $C_6H_5CH_2$, $(C_2H_5)_2NC_2H_4$, $(C_2H_5)_2NC_3H_6$;

(IIa) R = piperidyl-4;

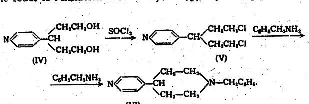
R' = H, $C_6H_5CH_2$, $(C_2H_5)_2NC_2H_4$



(III) R = pyridyl-4; R' = $(C_2H_5)_2NC_2H_4$

(IIIa) R = piperidyl-4; R' = $C_6H_5CH_2$

Reduction of (I) with lithium aluminum hydride leads to 3-(pyridyl-4')-1,5-dihydroxypentane (IV), which by treatment with thionyl chloride is transformed into 3-(pyridyl-4')-1,5-dichloropentane (V). Reaction of the latter with benzylamine leads to formation of N-benzyl-4-(pyridyl-4')-piperidine (VI):



(I) is hydrogenated in presence of platinum black with formation of the diethyl ester of β-(piperidyl-4)-glutaric acid (Ia) which is transformed by the above-described scheme via the corresponding diamides (IIa) into derivatives of diaminopentane (IIIa). An alternative to the above synthesis of diamides (IIa) is the reaction between the hydrochloride of β-(piperidyl-4)-glutaryl chloride with the appropriate amines.

EXPERIMENTAL

β-(Pyridyl-4)-glutaric acid. 3 g of the diethyl ester of β-(pyridyl-4)-glutaric acid (I) was heated at the boiling point for 8 hours with 23 ml of 1 N aqueous caustic potash solution. The cooled solution was treated with 22.8 ml of 1 N hydrochloric acid and evaporated down. From the dry residue which was a mixture of β-(pyridyl-4)-glutaric acid and potassium chloride, the acid was extracted with hot alcohol. After the alcohol was driven off in vacuum, we obtained 2.35 g (99%) of acid which was a white crystalline powder, soluble in water, alcohol and insoluble in ether, benzene, chloroform. M.p. 183-185°.

Found %: N 6.32, 6.68. $C_{10}H_{11}O_4N$. Calculated %: N 6.68.

Dihydrazide of β-(pyridyl-4)-glutaric acid. A solution of 3 g of ester (I) and 3 ml of hydrazine hydrate in 10 ml of alcohol was heated for 4 hours at the boil. Upon cooling the solution, crystals came down; they were rubbed with ether and filtered off. Yield 2.45 g (91.5%). The colorless crystals were readily soluble in water, alcohol, and insoluble in ether. M. p. 189-190°.

Found %: N 29.66. $C_{10}H_{15}O_2N_5$. Calculated %: N 29.52.

Diamide of β-(pyridyl-4)-glutaric acid. A mixture of 7 g of the diethyl ester of β-(pyridyl-4)-glutaric acid (I), 70 ml of alcohol and 70 ml of 29% ammonia solution was shaken for 25 hours. After this period had elapsed, the reaction mass was evaporated down in vacuum, the residue was rubbed with ether and the precipitate which came down was filtered off. We obtained 4.65 g (84.8%) of the diamide in the form of colorless crystals, readily soluble in water, difficulty soluble in alcohol and insoluble in ether and benzene. M.p. 192-194° (from alcohol).

Found %: C 57.24; H 6.43. $C_{10}H_{13}O_2N_3$. Calculated %: C 57.47; H 6.23.

Dibenzylamide of β-(pyridyl-4)-glutaric acid. 5 g of ester (I) and 10.2 g of benzylamine were heated at the boil for 20 hours. The crystalline dibenzylamide came down upon cooling the solution. For separation from the excess benzylamine the reaction mass was diluted with ether, the crystals were filtered off and washed with ether. Yield 6.2 g (92.3%). The compound was in the form of colorless crystals, soluble in alcohol, acetone, pyridine, and insoluble in water, benzene, ether. M.p. 152-153°.

Found %: C 74.31; H 6.30; N 10.61. $C_{24}H_{25}O_2N_3$. Calculated %: C 74.42; H 6.46; N 10.85.

Di-(diethylaminoethylamide) of β-(pyridyl-4)-glutaric acid. From 3 g of (I) and 8 g of diethylaminoethylamine by the above-described method we obtained 4 g of substance (87%) in the form of colorless crystals, soluble in water, chloroform, benzene, alcohol. M. p. 100-102°.

Found %: C 65.32; H 9.40; N 17.45. $C_{22}H_{39}O_2N_5$. Calculated %: C 65.18; H 9.63; N 17.28.

Di-(diethylaminopropylamide) of β-(pyridyl-4)-glutaric acid. From 2 g of (I) and 1.96 g of diethylaminopropylamine we prepared 1 g of the di-substituted amide, boiling range 220-250° (0.3 mm). The compound was in the form of faintly yellowish hygroscopic crystals, readily soluble in water and in organic solvents.

Found %: C 66.14; H 9.63. $C_{24}H_{43}O_2N_5$. Calculated %: C 66.45; H 9.87.

1,5-Di-(diethylaminoethylamine)-3-(pyridyl-4')-pentane. A solution of 3 g of the di-(diethylaminoethylamide) of β-(pyridyl-4)-glutaric acid in 80 ml of benzene was added in the course of 20 minutes to a suspension of 1.04 g of lithium aluminum hydride in 30 ml of anhydrous ether. The reaction mass was then heated at the boil for 20 hours, cooled and treated with 2 ml of water at 0°. Lithium and aluminum hydroxides were filtered off and carefully washed with benzene. After the benzene was driven off, the residue was vacuum-distilled. It boiled at 193-197° (0.4 mm). Yield 1.5 g (58%). The yellow oily liquid was readily soluble in water and in organic solvents, n_D^{18} 1.5047.

Found %: N 18.20. $C_{22}H_{43}N_3$. Calculated %: N 18.56.

Picrate – bright yellow crystals, m.p. 103-105°.

Di-(diethylaminoethyl) ester of β-(pyridyl-4)-glutaric acid. A small piece of metallic sodium was dissolved with mild heating (50-60°) in 15 ml of diethylaminoethanol. 3 g of the diethyl ester of β-(pyridyl-4)-glutaric acid (I) in 5 ml of diethylaminoethanol was added to the prepared solution of alcoholate in diethylaminoethanol and the reaction mixture was heated at 148-150° for 3 hours while the ethyl alcohl was concurrently expelled. The solution was then cooled, treated with 50% potash solution and extracted with ether. The ethereal extracts were dried over calcined potash, the ether was driven off, and the residue was vacuum-distilled. B.p. 195-197° (0.2 mm). Yield 2.95 g (64.3%). The diester was a colorless, viscous liquid, readily

soluble in organic solvents and in water.

Found %: C 64.51; H 8.9; N 10.09. $C_{22}H_{37}O_4N_3$. Calculated %: C 64.86; H 9.10; N 10.04.

3-(Pyridyl-4')-1,5-dihydroxypentane (IV). A solution of 6 g of ester (I) was added in the course of 30 minutes to a suspension of 3.54 g of lithium aluminum hydride in 60 ml of anhydrous benzene. The reaction mass was heated for 2 hours at the boil, cooled, and treated with 6.54 ml of water. The precipitated lithium and aluminum hydroxides were filtered off and repeatedly washed with dry pyridine. After the pyridine was driven off in vacuum, the crystalline residue was carefully washed with ether. We obtained 3.5 g of substance (86%) in the form of white crystalline powder, moderately soluble in water, alcohol, acetone, readily soluble in pyridine, and difficultly soluble in ether and benzene. M.p. 64-66°.

Found %: N 7.99, 7.72. $C_{10}H_{15}O_2N$. Calculated %: N 7.73.

3-(Pyridyl-4')-1,5-dichloropentane (V). An alcoholic solution of hydrogen chloride was added to 1.9 g of 3-(pyridyl-4')-1,5-dihydroxypentane until the appearance of an acid reaction on Congo. The alcohol was driven off in vacuum and the residue was dissolved in 12 ml of dry chloroform. 12 ml of thionyl chloride was added drop-wise to the chloroform solution of the diol hydrochloride. The reaction mass was heated at the boil for 1 hour, the chloroform and thionyl chloride excess were driven off in vacuum, the residue was treated with 50% potash solution and the oily dichloride which formed was extracted with chloroform. The chloroform solution was dried with sodium sulfate, the chloroform was driven off and the residue was vacuum-distilled. B.p. 121-122° (0.35 mm). Yield 0.85 g (42.7%). The colorless mobile liquid was readily soluble in water. Upon standing at room temperature, and also upon heating, it formed the quaternary salt which was insoluble in ether.

Found %: Cl 32.09. $C_{10}H_{14}NCl_2$. Calculated %: Cl 32.57.

N-Benzyl-4-(pyridyl-4')-piperidine (VI). 0.85 g of 3-(pyridyl-4')-1,5-dichloropentane and 10 ml of benzylamine were heated at the boil for 7 hours. The excess of benzylamine was driven off in vacuum and the residue was treated with 50% potash solution and extracted with ether; the ethereal solution was dried with potash, the ether was driven off, and the resulting substance was vacuum-distilled. B.p. 160-164° (0.3 mm). The yellow mobile oil was readily soluble in organic solvents and insoluble in water; n_D^{23} 1.5733.

Found %: C 80.85; H 7.77; N 10.94. M 244. $C_{17}H_{20}N_2$. Calculated %: C 81.00; H 7.95; N 11.20. M 252.

Picrate – bright yellow crystals, m.p. 215-216°.

Diethyl ester of β-(piperidyl-4)-glutaric acid (Ia). 22.2 ml of 21% alcoholic hydrogen chloride solution, 300 ml of anhydrous alcohol and 0.7 g of PtO_2 were added to 34 g of ester (1). The reaction mixture was shaken with hydrogen for 30 hours. In this time, a quantity of hydrogen was absorbed, sufficient to convert the pyridine ring to piperidine. When the absorption of hydrogen ceased, the alcohol was driven off in vacuum, the remaining hydrochloride was treated with 50% potash solution and the base was extracted with ether. The ethereal solution was dried with sodium sulfate, the ether was driven off, and the residue was vacuum-distilled. B.p. 131-132° (0.1 mm). Yield 31.5 g (93%). The colorless mobile liquid was readily soluble in water and in organic solvents; n_D^{18} 1.4688.

Found %: C 61.53; H 9.24; N 5.21. $C_{14}H_{25}O_4N$. Calculated %: C 61.79; H 9.22; N 5.20.

β-(Piperidyl-4)-glutaric acid. 2 g of the ester (Ia) and 14.7 ml of 1 N aqueous caustic soda solution was heated for 8 hours at the boiling point. The reaction mass was cooled to 80° and mixed with a solution of 2.25 g of silver nitrate, heated to the same temperature. The silver salt which came down was separated, washed with water, and dried. We obtained 3 g of salt. A suspension of the silver salt in 30 ml of water was saturated with hydrogen sulfide at 50° and the reaction mass was then cooled, treated with carbon, the silver sulfide and carbon were filtered off, and the aqueous solution of β-(piperidyl-4)-glutaric acid was evaporated to dryness in vacuum. We obtained 1 g (63.8%) of acid in the form of colorless crystals, readily soluble in water, insoluble in alcohol and ether. M. p. 213°.

Found %: N 6.58. $C_{10}H_{17}O_4N$. Calculated %: N 6.52.

Hydrochloride – colorless crystals, readily soluble in water and in alcohol, insoluble in ether, acetone, benzene. M.p. 174-175°.

Found %: Cl 14.72. $C_{10}H_{17}O_4N \cdot HCl$. Calculated %: Cl 14.22.

Diamide of β-(piperidyl-4)-glutaric acid. Upon treatment with ammonia by the above-described method, from 2 g of diethyl ester of β-(piperidyl-4)-glutaric acid (Ia), we obtained 0.8 g of the diamide (51%) in the form of white crystalline powder, readily soluble in water, alcohol, and insoluble in ether. M.p. 186° (from alcohol-ether mixture).

Found %: C 56.03; H 8.85. $C_{10}H_{19}O_2N_3$. Calculated %: C 56.33; H 8.92.

Dibenzylamide of β-(piperidyl-4)-glutaric acid. A) 2 g of the diethyl ester of β-(piperidyl-4)-glutaric acid and 10 g of benzylamine were heated at the boil for 40 hours. After the benzylamine was driven off in vacuum, yellowish crystals remained. These were filtered off, washed with ether, and recrystallized from alcohol. Yield 2 g (69%). The colorless crystals were readily soluble in alcohol, chloroform, and insoluble in ether, water, benzene. M.p. 163-167°.

Found %: N 10.24. $C_{24}H_{31}O_2N_3$. Calculated %: N 10.64.

B) 2 g of the hydrochloride of β-(piperidyl-4)-glutaric acid and 9 ml of thionyl chloride were heated for 2 hours at 50-55°. During this period of time the precipitate of the hydrochloride dissolved. Thionyl chloride was driven off in vacuum, the hydrochloride of the dichloride of β-(piperidyl-4)-glutaric acid was mixed with 50 ml of anhydrous ether and, upon cooling, was added to an ethereal solution of 5 g of benzylamine. The reaction mass was treated with 50% potash solution and extracted with chloroform. After the chloroform had been expelled, the residue was rubbed with ether, the crystals were filtered off, washed with ether, and dried. M.p. 167°. Yield 1 g (54%).

Di-(diethylaminoethylamide) of β-(piperidyl-4)-glutaric acid. From 3 g of the diethyl ester of β-(piperidyl-4)-glutaric acid and 10 g of diethylaminoethylamine, we obtained 2.5 g (57%) of substance, boiling range 170-190° (0.4 mm). The yellow viscous liquid was readily soluble in organic solvents and difficultly soluble in water.

Found %: C 63.30, 63.40; H 10.45, 10.50. $C_{22}H_{45}O_2N_5$. Calculated %: C 63.23; H 10.92.

1,5-Dibenzylamino-3-(piperidyl-4')-pentane. A mixture of 2 g of the dibenzylamide of β-(piperidyl-4)-glutaric acid, 0.8 g of $LiAlH_4$, 40 ml of dry ether and 60 ml of dry dioxane, was heated at 70° for 20 hours. After the usual treatment, we obtained 0.7 g (38%) of substituted 1,5-diaminopentane in the form of light yellow, rather viscous liquid, readily soluble in organic solvents and difficultly soluble in water. Boiling range 255-270° (0.5 mm).

Found %: N 11.23. $C_{24}H_{35}N_3$. Calculated %: N 11.50.

SUMMARY

A series of derivatives of β-(pyridyl-4)-and β-(piperidyl-4)-glutaric acids and products of their transformations were synthesized: substituted 3-(pyridyl-4')-1,5-diaminopentanes and 3-(piperidyl-4')-1,5-diaminopentanes, 3-(pyridyl-4')-1,5-dichloropentane, N-benzyl-4,4'-pyridino-piperidine.

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* T.p. = C. B. Translation pagination.

SOME PRODUCTS OF TRANSFORMATION OF TETRALIN HYDROPEROXIDE

A. I. Kamneva and L. A. Salmin

The primary products of oxidation of hydrocarbons – peroxides – have been adequately studied by a number of Russian and foreign scientists [1,3]. However, the further transformations of peroxides and their role in resinification have remained uninvestigated.

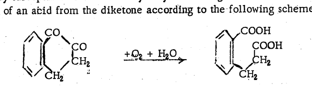
The present work is devoted to a study of the mechanism of transformation of tetralin hydroperoxide in the process of oxidation.

Tetralin hydroperoxide was first prepared by Hartman and Seiberth in 1932 [2]; it was identified by Hock and Susemihl [3], and studied more closely by Ivanov [1] and Medvedev [4]. Medvedev showed further oxidation of tetralin hydroperoxide leads to breakdown to a ketone – tetralone. Apart from the hydroperoxide and tetralone, Medvedev indicates the possibility of formation of a hydroxyalkyl peroxide as a product of reaction of tetralone with the hydroperoxide. It was later shown by Robertson and Waters [5] that the main products of autoxidation of tetralin are α-tetralone, α-tetralol and an acidic substance obtained by oxidation of tetralone.

In our preceding studies [6, 7] we showed, independently of Robertson and Waters, that among the products of oxidation of tetralin, apart from the hydroperoxide and tetralone, are a diketone, an acid and resinified substances. An alcohol (tetralol) was not detected among the products of oxidation of tetralin; evidently the previous investigators mistook the enolic form of tetralone for an alcohol. We demonstrated the tautomeric character of tetralone in a special paper devoted to this problem [6].

In the present communication we bring forward data on the investigation of one of the products of autoxidation of tetralin – the diketone – and its further transformations. Analysis of the diketone and of the derivatives obtained showed that this α-diketone is 3,4-dihydro-1,2-naphthoquinone, not previously described in the literature. This diketone is very unstable and when stored for 3 months it darkens and becomes viscous; its acid number rises from 15 mg KOH/g substance to 165 mg KOH/g substance. Analysis revealed the presence in this diketone of 55% acids, from which was isolated β-o-carboxyphenylpropionic acid. We therefore conclude that the acids are formed from the diketone by reaction with oxygen and moisture from the air during storage.

Examination of the literature on this problem, in particular the papers of M. M. Shemyakin [8], indicate that the presence of ketonic groups promotes oxidative-hydrolytic cleavage of molecules and especially of molecules of α-diketones in which they are in the ortho-position. In this case the carbon bond is very strongly polarized and is readily susceptible to oxidative-hydrolytic cleavage with formation of a dibasic acid. Consequently the formation of an acid from the diketone according to the following scheme may be considered proved:



3,4-dihydro-1,2-naphthoquinone β-o-carboxyphenylpropionic acid

EXPERIMENTAL

I. Preparation of properties of 3,4-dihydro-1,2-naphthoquinone. Diketone fractions, obtained upon distillation of oxidized tetralin, distilled over at 114-116° (1.5 mm). In order to study the properties of the diketone, these fractions were purified by 3-fold vacuum-distillation.

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B.p. 114° (1.5 mm), d_4^{20} 1.1515, n_D^{20} 1.5460, MR_D 43.08; calculated 42.61.

Found %: C 75.16; H 5.22. $C_{10}H_8O_2$. Calculated %: C 74.99; H 5.03.

2,4-Dinitrophenylhydrazone. A solution of the reagent was added to a weighed portion of the diketone dissolved in ethyl alcohol. Lustrous orange crystals immediately came down and were filtered after 2 hours, washed with alcohol and dried. M.p. 137-138°. Analysis showed this substance to be the mono-derivative of the α-diketone.

Found %: C 56.32; H 3.46; N 16.27. $C_{16}H_{12}O_5N_4$. Calculated %: C 56.47; H 3.53; N 16.47.

After 2 days, dark cherry-colored crystals formed in the filtrate, m.p. 260°. The percentage composition corresponded to that of the di-derivative of the α-diketone.

Found %: C 49.50; H 3.23. $C_{22}H_{16}O_8N_8$. Calculated %: C 50.77; H 3.08.

The phenylhydrazone was obtained in the form of fine white needles, m.p. 132°.

Found %: N 10.89. Calculated for mono-derivative %: N 11.20.

Reaction with o-phenylenediamine yielded the quinoxaline derivative in the form of fine silvery-white needles, m.p. 152.5.

Found %: N 10.85. $C_{16}H_{12}N_2$ · Calc. %: N 12.07.

II. Conversion of diketone upon standing in air. After 3 months, the pure diketone became very viscous, had a dark cherry color and had started to crystallize. Its acidity rose from 15 mg KOH/g of compound (due to enolization of the diketone) to 165.2 mg KOH/g of compound.

For analysis we took 6.6958 g of product. Vacuum-distillation yielded two fractions: 1st, b.p. 116-117°, 1.5613 g, diketone; 2nd, boiling range 136-140°, 1.6612 g, β-o-carboxyphenylpropionic acid. After distillation the very viscous, almost black residue could be stretched out into threads. The residue was dissolved in ether and treated with 5% $NaHCO_3$ in order to extract the unexpelled acids, of which there remained 2.0315 g.

Thus, upon standing, a total of 1.5613 g (23.35%) of diketone remained unchanged, 3.6927 g (55.13%) of acids separated out and 1.4418 g (31.52%) of neutral resinous residue formed. From the acid portion, we isolated and identified β-o-carboxyphenylpropionic acid, m.p. 163.5°. We prepared its silver salt.

Found %: Ag 53.53. $C_{10}H_8O_4Ag_2$. Calculated %: Ag 52.94.

SUMMARY

1. The presence in the products of oxidation of tetralin of 3,4-dihydro-1,2-naphthoquinone is demonstrated.

2. It is established that β-o-carboxyphenylpropionic acid is a product of oxidative-hydrolytic cleavage of 3,4-dihydro-1,2-naphthoquinone.

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*T.p. = C.B. Translation pagination

SULFONATION AND SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

XXV. APPLICATION OF DIOXANE-SULFOTRIOXIDE TO THE DETERMINATION OF MONO- AND POLYHYDROXY COMPOUNDS

A.P. Terentyev and N.B. Kupletskaya

Preceding communications in this series concerned mainly reactions of substitution of hydrogen by the sulfo group in compounds that easily resinified in presence of the usual sulfonating agents. Examples of such acidophobic (towards sulfuric acid) compounds are diverse hydroxy compounds. The carbonization of sugar under the action of concentrated sulfuric acid is well-known. Many less complex hydroxy compounds readily dehydrate with formation of olefins. If, however, the complex of sulfur trioxide with dioxane is used as sulfonating agent, then the process of sulfonation, i.e., formation of an acid ester of sulfuric acid, proceeds without any trace of resinification.

In studying the sulfonation of polyhydroxy compounds, we decided to apply this reaction to the quantitative determination of hydroxyl groups. The method is based on the irreversible reaction [1]:

$$ROH + O(CH_2CH_2)O \cdot SO_3 \rightarrow ROSO_3H + O(CH_2CH_2)_2O.$$

Under the action of water, dioxane-sulfotrioxide immediately gives sulfuric acid $O(CH_2CH_2)_2O \cdot SO_3 + H_2O \rightarrow H_2SO_4 + O(CH_2CH_2)_2O$, which can be readily back-titrated with sodium carbonate or alkali with the usual indicators, since dioxane does not interfere with the titration.

We see that on reaction with alcohols only one of the two acid equivalents of sulfur trioxide is lost, and this gives us the possibility of determining hydroxyl groups.

It was decided to work out specific conditions for carrying out the sulfonation reaction in order to utilize it for analysis. The reagent used was 1.5-2 N solution of sulfur trioxide in dioxane. Sulfonation must be carried out with a 3-4-fold excess of sulfur trioxide (calculated for each hydroxyl). After dilution of the reaction mixture with water, it is necessary to carry out the titration with the utmost speed since the acid esters of sulfuric acid are hydrolyzed with great facility. For titration we used indicators that changed color in an acid medium: Congo red, bromophenol blue, and methyl orange. Unfortunately, the solution of sulfur trioxide in dioxane is not very stable, and there is an appreciable change of titer even when kept in sealed ampoules. However, the solution is quite suitable for analysis in the course of two to three days.

Procedure

Dioxane - sulfotrioxide solution. Commercial dioxane was dried over calcium chloride and distilled. The solution of dioxane-sulfotrioxide was made up in an apparatus consisting of two wash-bottles connected in series and a gasholder filled with air. A stream of air passing through the first wash-bottle, filled with 60% oleum, carried with it sulfur trioxide into the second wash-bottle containing dioxane. Passage of air was continued until a white precipitate of dioxane-sulfotrioxide, insoluble on shaking, had formed in the second wash-bottle. A little dioxane was then added to dissolve the precipitate completely. In this manner a 1.5-2 N solution was prepared. The dioxane solution was measured out with a small (1.5 ml) pipet with two graduation marks. The pipet was constructed from thick barometric glass with an internal diameter of about 1.5 mm. To the top of the pipet was attached a rubber tube in which was inserted a glass bead serving as a seal. The rubber tube was joined to a system of communicating vessels, movement of which enabled the solution to be run from the pipet. These communicating vessels were filled with saturated calcium chloride solution. The lower end of the pipet was slightly curved, and on it was attached, with a rubber stopper, a small conical flask to protect the pipet against moisture and dirt.

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Method of determination. A weighed amount of the substance (0.02-0.05 g) was transferred in the usual manner into a dry, 50 ml conical flask fitted with a ground-glass stopper; a measured volume of dioxane-sulfotrioxide solution was added and the mixture left for 2-3 minutes. Samples of solid substances were left until completely dissolved. Samples of volatile substances were put directly into a measured volume of sulfur trioxide solution. About 10 ml water was added, the indicator was introduced, and rapid titration at once effected with sodium carbonate solution until the color of the indicator changed. A blank titration was run in parallel: titration of a measured volume of dioxane-sulfotrioxide after dilution with water. The period for each determination was about 10 minutes.

The following formula was used for calculation:

$$\%H_{act.} = \frac{(a-b)\cdot N}{10\cdot S}; \quad \text{Amount of } H_{act.} \text{ (in moles)} = \frac{M\cdot\%H_{act.}}{100},$$

where a is the number of milliliters of sodium carbonate solution required for titration in the blank experiment; b is the number of milliliters of sodium carbonate solution for titration after reaction with the sample; N is the normality of the sodium carbonate; S is the weight of the sample; M is the molecular weight of the sample of substance.

The determinations were accurate on the average to ± 2-3%. Results of determinations are set forth in Table 1.

We see that satisfactory results are obtained not only for primary and secondary alcohols but also for tertiary alcohols. This is an important observation because the usual methods of acetylation and phthalation do not permit determination of tertiary alcohols.

TABLE 1

Substances investigated	Percent $H_{act.}$ calculated	Percent $H_{act.}$ found	OH (in moles)
Monohydric alcohols			
Ethanol	2.19	2.20	1.01
Butanol-1	1.36	1.33	0.98
2-Methylpropanol-3	1.36	1.30	0.97
2-Methylpropanol-4	1.14	1.12	0.99
Nonanol-1	0.70	0.68	0.98
Allyl alcohol	1.73	1.76	1.02
1,1,1-Trichloropropanol-2	0.62	0.56	0.92
Benzyl alcohol	0.93	0.92	0.99
Phenylpropyl alcohol	0.74	0.73	0.99
Octanol-2	0.77	0.77	1.00
Cyclohexanol	1.00	1.00	1.00
Menthol	0.64	0.64	1.00
2-Methylbutanol-2	1.14	1.14	1.00
2-Methylhepten-4-ol-2	1.00	0.93	0.93
2-Methylhexanol-2	0.86	0.86	1.00
$CH_2CH_2OCH_2C(OH)\cdot C_5H_{11}$	0.64	0.64	1.00
Polyhydric alcohols			
Butanediol-1,3	2.23	2.26	2.03
Butanediol-1,4	2.23	2.23	2.00
Butynediol-1,4	2.34	2.30	1.99
Pinacone	1.70	1.72	2.03
Pentaerythritol	2.96	2.96	4.00
Mannitol	3.31	3.26	5.96

When analyzing such polyhydroxy compounds as pentaerythritol or mannitol, the samples are finely pulverized and subjected to the action of the reagent until completely dissolved (approximately 1-2 hours). The blank experiment is run in parallel for the same period.

Cases have occurred in which the method did not give satisfactory results. These involve secondary and tertiary aromatic alcohols and phenols, the acid esters of which are evidently very easily hydrolyzed. Thus, triphenylcarbinol almost completely "fails to titrate", and methylbenzyl carbinol, phenol and hydroquinone only titrate to the extent of 50-80%.

TABLE 2

Substances investigated	Percent $H_{act.}$ calculated	Percent $H_{act.}$ found	OH (in moles)
Glucose	2.79	2.76	4.97
Galactose	2.79	2.79	5.00
Fructose	2.24	2.19	3.94

Determinations were also made of the number of hydroxyl groups in some sugars. Results are presented in Table 2.

Oximes also contain an active hydrogen atom; they should therefore react with sulfur trioxide to give the corresponding ester. It is known, however, that acid reagents easily cause rearrangements and transformations of oximes. Aldoximes isomerize and split off water with particular ease; we could therefore have expected lower analytical results for them. Ketoximes are not susceptible to dehydration and should therefore give better results. These assumptions are confirmed experimentally (Table 3).

TABLE 3

Substances investigated	Percent $H_{act.}$ calculated	Percent $H_{act.}$ found	OH (in moles)
Ketoximes			
Acetoxime	1.38	1.36	0.99
Acetophenoneoxime	0.74	0.71	0.96
Benzoin oxime (cuprone)	0.89	0.91	2.06
Aldoximes			
Benzaldoxime (syn)	0.83	0.53	0.71
Benzaldoxime (anti)	0.83	0.70	0.84
o-Nitrobenzaldoxime (syn)	0.61	0.47	0.78
o-Nitrobenzaldoxime (anti)	0.61	0.50	0.83

Investigation of other classes of compounds showed that under the conditions of determination, esters of mono- and dibasic saturated and unsaturated acids do not alter the titer of dioxane-sulfotrioxide. This was confirmed for the case of ethyl acetate, methyl methacrylate and dimethyl fumarate. The same is true of nitriles and amides of acids. Benzyl cyanide, acrylonitrile, acetamide and acetanilide all failed to react under our conditions with sulfur trioxide solution. This is an important observation, since the presence of all these groupings markedly interferes with the determination of active hydrogen by the Chugaev-Tserevitinov [2] and lithium aluminum hydride methods [3]. The nitro group, which interferes with determinations by methods using methyl magnesium iodide and lithium aluminum hydride, does not react with dioxane-sulfotrioxide, as was found in the case of nitromethane.

SUMMARY

1. A method was developed for titrimetric determination of hydroxyl groups with the help of dioxane-sulfotrioxide. The accuracy of the method is ± 2-3%.

2. Satisfactory results were obtained for mono- and polyhydric alcohols, sugars and ketoximes.

3. It was shown that phenols and aldoximes cannot be determined by this method.

4. Nitrile, ester and amide groups and the nitro group do not change the titer of dioxane-sulfotrioxide under the conditions of determination.

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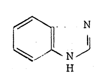
IMIDAZOLE DERIVATIVES

XIV. OXIDATION OF BENZIMIDAZOLE AND ITS METHYL DERIVATIVES*

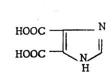
L. S. Efros, N. V. Khromov-Borisov, L. R. Davidenko and M. M. Nedel

Earlier it was shown [1, 2] that a disturbance of the equality of the bonds exists in the benzene ring of benzimidazole (I), in its character close to that already known for a long time in naphthalene. This disturbance of bond equality should considerably weaken the stability of the benzene ring found in benzimidazole. On the other hand, the imidazole ring, entering into this molecule, shows high stability. The latter can be observed, for example, in the hydrogenation reaction, where, even under extremely drastic conditions, benzimidazole (I) forms only the 4,5,6,7-tetrahydro derivative [3].

It also seemed of interest to compare the stability of the rings, forming this molecule (I), in the oxidation reaction; in this connection an attempt could be made to find a method possessing practical value for the preparation of imidazole-4,5-dicarboxylic acid (II), used for the synthesis of imidazole [4] and of certain dyes [5].



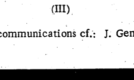
(I)



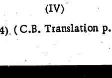
(II)

Bamberger and Berle [6] occupied themselves with oxidation of (I) long before we did. However, due to the fact that they ran this reaction in alkaline medium, in which hetero rings are usually less stable [7], the yield of the dicarboxylic acid (II) in their numerous experiments failed to exceed 1%.

Proceeding from the above, we ran the oxidation of (I) in acid medium with chrome mixture; here we obtained the dicarboxylic acid (II) in about 60% yield. As a result, both in the oxidation in acid medium and in hydrogenation of the two rings forming the benzimidazole molecule (I), the more stable, and consequently the more aromatic, is not the benzene ring, but instead it is the imidazole ring. It also seemed of interest to study the oxidation of 2-methylbenzimidazole (III) and of 1-methylbenzimidazole (V). The methyl group in the 2-position of the imidazole molecule is extremely passive in oxidation reactions (as we had already repeatedly observed earlier [2, 8]), and consequently it could be expected that the action of the oxidizing agent would be directed mainly toward the benzene ring. Experiment confirmed our expectations. It was found that the oxidation of Compound (III) with chrome mixture under analogous conditions gave 2-methylimidazole-4,5-dicarboxylic acid (IV) in 50% yield.



(III)



(IV)

* For previous communications cf.: J. Gen. Chem. 24, 488 (1954) (C.B. Translation p. 497).

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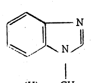
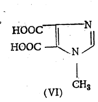
It is extremely interesting that this remarkable stability of the methyl group in (III) with respect to the action of oxidizing agents is coupled with the presence of mobility for its hydrogen atoms, established by A. E. Porai-Koshits [9].



(V)



(VI)

The experiments on the oxidation of 1-methylbenzimidazole (V) with chrome mixture revealed, in contrast to the previous cases, that it is impossible to obtain 1-methylimidazole-4,5-dicarboxylic acid (VI) by this method. We synthesized this acid (VI) by a different method, and specifically, by the methylation of imidazole-4,5-dicarboxylic acid (II) with dimethyl sulfate. [On the basis of studying the properties of the previously unknown 1-methylimidazole-4,5-dicarboxylic acid (VI) we attempted to isolate it from the oxidation products of 1-methylbenzimidazole (V) with chrome mixture and found that it is not contained in the reaction mixture.] As a result, replacement of the hydrogen in the imino group of the imidazole ring in benzimidazole by the methyl group, preventing tautomerization [10], weakens the stability of the imidazole ring toward oxidation.

In the potentiometric titration of the dicarboxylic acids (II), (IV) and (VI) we obtained curves with distinct jumps in the potentials, characterizing the acidity of their carboxyl groups. The values of the acid dissociation constants found from these curves are given in Table 1. The titration data obtained for the dicarboxylic acid (VI) support the structure assigned to it.

TABLE 1

Dicarboxylic Acid	K_1	K_2
(II)	$10^{-4.0}$	$10^{-7.8}$
(IV)	$10^{-4.2}$	$10^{-8.0}$
(VI)	$10^{-3.9}$	$10^{-8.0}$

TABLE 2

Concentration of sulfuric acid (%)	Yield of imidazole-4,5-dicarboxylic acid (II) (in g)	(in %)
50	0.56	42.5
55	0.62	47
60	0.75	57
65	0.92	70
70	0.89	67.5
75	0.89	67.5

EXPERIMENTAL

Oxidation of benzimidazole (I). At first, in order to determine the optimum acidity for the medium, we studied the oxidation of (I) with chromic anhydride. For the reaction we took solutions of 1 g of the product in 35 ml portions of sulfuric acid of various concentrations, and the oxidation was with 5.6 g of chromic anhydride and mild boiling of the reaction mixture. The experimental results are given in Table 2.

The following procedure is recomended for the practical preparation of dicarboxylic acid (II): oxidation of benzimidazole (I) was performed in 350–450 ml porcelain beaker with continuous mechanical stirring. 5 g of benzimidazole was dissolved in a mixture of 70 ml of concentrated sulfuric acid (d 1.83) and 55 ml of water, and the liquid was heated to 90° and addition in small portions of 37 g of well ground potassium dichromate was begun. The reaction evolved heat and was accompanied by moderate foaming. The potassium dichromate was added at the rate necessary to maintain the temperature of the reaction mixture in the range 90–95°. After all the potassium dichromate was added (average time 40–50 minutes), the reaction mixture was stirred for 10–15 minutes more and then poured in 400 ml of water and the total reaction mass was externally cooled with cold water. After 30–40 minutes, the prepared dicarboxylic acid (II) was filtered off, washed with water and dried. The yield was 55–57%. The product was purified by two-fold reprecipitation from the alkaline solution with acid. (The acid was added to the alkaline solution heated to the boiling point and previously treated with activated carbon for a half hour).

The dicarboxylic acid (II) was difficultly soluble in organic solvents and very difficultly soluble in hot water. It decomposed with frothing at about 290°. (The capillary was placed in a melting-point determination apparatus which was heated to 270°. The temperature then was raised at the rate of 1° per 7–8 seconds). We were able to crystallize (although not very well) dicarboxylic acid (II) from large quantities of dilute boiling hydrochloric acid (1:5).

0.1557 g of the acid was dissolved in 25 ml of 0.102 N caustic soda solution and the resulting solution was titrated in the presence of a glass electrode with 0.104 N hydrochloric acid solution. The magnitude of the pH at the half points was 4.0 and 7.8; 20.23 ml of hydrochloric acid were spent in the titration.

Found %: N 17.94, 18.12. M 148. $C_5H_4O_4N_2$. Calcd. %: N 18.06. M 156.

Oxidation of 2-methylbenzimidazole (III). Oxidation of (III) with a chromic mixture was performed by the same method as was the oxidation of (I). A yield of 51–53% of dicarboxylic acid (IV) was obtained. For purification, it was recrystallized from boiling water (1 g of acid to 200–225 ml of water) in the presence of activated carbon. After treatment, it was in the form of colorless needles which decomposed with frothing at around 270°. (A capillary with the compound was placed in melting-point determination apparatus, which was heated to 260°. The temperature was further raised at the rate of 1° per 7–8 seconds).

Dicarboxylic acid (II) was difficultly soluble in organic solvents and slightly soluble in hot water and in pyridine.

0.2268 g of the acid was dissolved in 40 ml of 0.102 N caustic soda solution and the resulting solution was titrated in the presence of a glass electrode with 0.104 N hydrochloric acid solution. The magnitude of the pH at the half points was 4.2 and 8.0; 25.17 ml of hydrochloric acid solution was spent in the titration.

Found %: N 16.40, 16.34. M 173. $C_6H_6O_4N_2$. Calcd. %: N 16.47. M 170.

Preparation of 1-methylimidazole-4,5-dicarboxylic acid (VI). 4.6 g of caustic soda was dissolved in 420 ml of water and then 6 g of dicarboxylic acid (II) and then 10 ml of dimethyl sulfate was added with continuous stirring. After 5–10 minutes, when the reaction mixture had become thoroughly transparent, 10 ml of concentrated ammonia solution was added to it; it was heated to a boil and then acidified with hydrochloric acid until acid reaction to Congo. Upon cooling to room temperature, the liquid was immediately filtered clear of the precipitate of unreacted dicarboxylic acid (II) and then evaporated to 30–40 ml volume. The next day the crystals that had formed were filtered off and recrystallized from 50 ml of water in the presence of activated carbon. The yield of dicarboxylic acid (VI) was 25–27%. It was obtained in the form of nacre-colored leaflets which decomposed with frothing around 262°. (A capillary with the compound was placed in a melting-point determination apparatus which was heated to 250°. The temperature was further raised at the rate of 1° per 7–8 seconds). Dicarboxylic acid (VI) was poorly soluble in organic solvents and quite readily soluble in hot water and in pyridine.

0.1988 g of the acid was dissolved in 100 ml of water and the resulting solution was titrated in the presence of a glass electrode with 0.10024 N caustic soda solution. The magnitude of the pH at the half points was 3.9 and 8.0; 23.0 ml caustic soda solution was spent in titration.

Found %: C 42.21, 42.17; H 3.55, 3.55; N 16.65, 16.38. M 172. $C_6H_6O_4N_2$. Calcd. %: C 42.35; H 3.53; N 16.47. M 170.

SUMMARY

1. Conveniently practical methods for the synthesis of imidazole-4,5-dicarboxylic and 2-methylimidazole-4,5-dicarboxylic acids were found by means of respectively oxidizing benzimidazole and 2-methylbenzimidazole with chrome mixture.

2. The destruction of the benzene ring, and not of the imidazole nucleus, in the oxidation of benzimidazole and 2-methylbenzimidazole with chrome mixture confirms once more the existence of the earlier described disturbance of the equality of the bonds in the benzene ring of the above-mentioned compounds.

3. The fact that it is impossible to obtain 1-methylimidazole-4,5-dicarboxylic acid by the oxidation of 1-methylbenzimidazole is evidence that the stability of the imidazole ring is associated with its ability to tautomerize.

4. A method for the preparation of 1-methylimidazole-4,5-dicarboxylic acid was described and some of its properties were studied.

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IMIDAZOLE SERIES

III. ACTION OF α-HALO KETONES ON 2-MERCAPTOIMIDAZOLES

P. M. Kochergin and M. N. Shchukina

It is known that thiourea, its N-substituted derivatives, and also the thioamides of carboxylic acids, react with α-halo ketones to yield thiazole derivatives. Here the intermediate compounds were not isolated, since these reactions proceed with vigor, and it is impossible to stop them at the first stage. 2-Mercaptoimidazoles can be regarded as being cyclic N, N'-disubstituted isothioureas; consequently it could be expected that derivatives of the little known imidazo-(2,1-b)-thiazole heterocyclic system would be obtained when they are reacted with α-halo ketones. It seemed of interest to isolate the intermediate compounds obtained in the formation of the thiazole ring—the 2-β-ketoalkyl (aryl)-mercaptoimidazoles, and to study their properties and the conditions for their transformation into imidazo-(2,1-b)-thiazoles.

In the present work we studied the reaction of the earlier synthesized 4(5)-phenyl- and 4 (5)-p-nitrophenyl-2-mercaptoimidazoles [1] with α-halo ketones of the fatty, fatty-aromatic and alicyclic series in alkaline, neutral and acid media. The reaction of 4 (5)-phenyl-2-mercaptoimidazole with chloroacetone, α-chloroethyl methyl ketone, 2-chlorocyclohexanone, α-bromoacetophenone and its para- and meta-nitro derivatives, and also of 4 (5)-p-nitrophenyl-2-mercaptoimidazole with chloroacetone, α-chloroethyl methyl ketone and 2-chlorocyclohexanone, in alcohol solution in the presence of an equivalent amount of alkali, gave the corresponding 2-β-ketoalkyl (aryl)-mercaptoimidazoles (I-IX, table) in good yields (86-98%). The 2-β-ketoalkyl (aryl)-mercaptoimidazoles are also formed when these reactions are run in aqueous alkali solution; however, in this case tarring is observed and their yield is greatly reduced. If the reaction is run in either alcohol or water solution (in the absence of alkali), then the corresponding hydrogen halide salts of the 2-β-ketoalkyl (aryl)-mercaptoimidazoles are obtained in good yields.

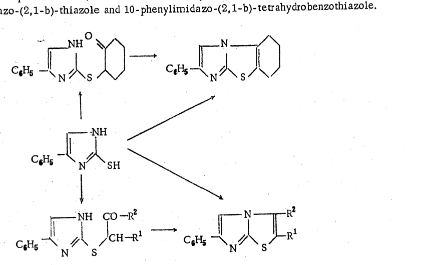
The ketonic properties of the 2-β-ketoalkyl (aryl)-mercaptoimidazoles are confirmed by their reaction with semicarbazide and with 2,4-dinitrophenylhydrazine, by their ease of bromination in the cold, and also by the presence of the absorption bands for the carbonyl group in the infrared spectrum (~ 1760 cm^{-1}) *.

The reaction of the 2-mercaptoimidazoles with the α-halo ketones of the fatty and alicyclic series proceeds differently in acid medium. The reaction of 4 (5)-phenyl-2-mercaptoimidazole with chloroacetone and with 2-chlorocyclohexanone in hydrochloric acid solution gave us imidazo-(2,1-b)-thiazole and imidazo-(2,1-b)-tetrahydrobenzothiazole derivatives, respectively: 3-methyl-6-phenylimidazo-(2,1-b)-thiazole and 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole. Under analogous conditions the fatty-aromatic α-halo ketones form hydrogen halide salts of 2-β-ketoarylmercaptoimidazoles.

The 2-β-ketoalkyl (aryl)-mercaptoimidazoles are intermediate compounds in the formation of the thiazole ring, since they are capable of cleaving one molecule of water and being converted into imidazo-(2,1-b)-thiazole derivatives. This reaction depends on the temperature and time of exposure to the reagent, the character of the ketone radical, the nature of the substituent in the 4 (5)-position of the imidazole ring, and also on the catalytic influence of hydrogen ions. Thus, for example, closure of the thiazole ring fails to proceed when 4 (5)-phenyl-2-acetonylmercaptoimidazole is boiled in 25% alcoholic hydrogen chloride solution, while at higher temperature (when boiled in hydrochloric acid) 3-methyl-6-phenylimidazo-(2,1-b)-thiazole is formed in 94% yield. Boiling with hydrochloric acid (11-38%) easily evokes the cyclization of 4 (5)-phenyl-2-β-ketoalkylmercaptoimidazoles, in which the radicals are the residues of either fatty or

* The spectrum for 4 (5)-phenyl-2-acetonylmercaptoimidazole was taken by Yu. N. Sheinker.

alicylic ketones (acetonyl, methylacetonyl, cyclohexanonyl). With this method, proceeding from the corresponding 2-β-ketoalkylmercaptoimidazoles, we obtained: 3-methyl-6-phenylimidazo-(2,1-b)-thiazole, 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole and 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole.



1) $R^1 = H$, $R^2 = CH_2COCH_3$; 2) $R^1 = R^2 = CH_3$.

The S-cyclohexanonyl derivative of 4 (5)-p-nitrophenyl-2-mercaptoimidazole fails to cyclize under analogous conditions, which, probably, can be explained by the insolubility of this compound in hydrochloric acid. The S-substituted derivatives of 4 (5)-phenyl-2-mercaptoimidazole with residues of fatty-aromatic ketones (phenacyl, para- and meta-nitrophenacyl) fail to suffer closure even on prolonged boiling in concentrated hydrochloric acid. To cyclize these compounds it is necessary to use powerful water-removing agents.

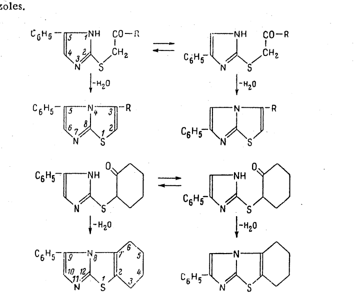
A study of the cyclization of 2-β-ketoalkylmercaptoimidazoles and of imidazo-(2,1-b)-thiazole derivatives permitted us to conclude that the formation of the thiazole ring proceeds under the catalytic influence of hydrogen ions. This conclusion is in accord with a number of known facts. For example, the condensation of carbonyl compounds with hydroxylamine, hydrazines and semicarbazides (i. e. with compounds containing either the amino or imino group) is catalyzed by mineral acids [2]. In nearly all cases the formation of thiazole derivatives, in particular, proceeding from thiourea, the thioamides of carboxylic acids, and α-halocarbonyl compounds, proceeds easily without need for neutralizing the hydrogen halide that is formed in the reaction. This also applies to the known S-acetonyl derivatives of 2-mercaptoimidazoles [3–5], 2-mercaptobenzimidazoles [5] and 8-mercaptopurines [3, 6], the cyclization of which to the corresponding bicyclic and tricyclic systems proceeds in the presence of acidic reagents (glacial acetic acid, concentrated sulfuric acid, or phosphorus oxychloride).

The catalytic influence of hydrogen ions in the closure of the thiazole ring is supported by the following. Imidazo-(2,1-b)-thiazole derivatives are formed when 4(5)-phenyl-2-mercaptoimidazole is heated with α-halo ketones of either the fatty or alicyclic series in hydrochloric acid, while in aqueous (either alkaline or neutral) solution 4(5)-phenyl-2-β-ketoalkylmercaptoimidazoles are obtained. When boiled in water the latter fail to cyclize, while in hydrochloric acid at the same temperature they are transformed into imidazo-(2,1-b)-thiazole derivatives. The boiling of 4(5)-phenyl-2-acetonyl- and 4(5)-phenyl-2-(α-methyl) acetonylmercaptoimidazoles in normal butyl alcohol fails to alter these compounds, while their hydrochlorides under the same conditions are almost quantitatively converted into the hydrochlorides of the cyclic compounds: 3-methyl-6-phenylimidazo-(2,1-b)-thiazole and 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole.

A similar example was described in the literature: the condensation of 8-mercaptotheophylline with chloroacetone in anhydrous alcohol in the presence of sodium ethylate gave 8-acetonylmercaptotheophylline, while when the heating was done in the same solvent without sodium alcoholate (i. e. under conditions excluding the neutralization of the acid formed) the corresponding purino-(8,7-b)-thiazole was obtained [3].

It should also be mentioned that the 4(5)-phenyl- and 4(5)-p-nitrophenyl-2-β-ketoalkyl (aryl)-mercaptoimidazoles obtained by us fail to show cyclization when heated in solutions of alkaline metal carbonates, while when heated in sodium hydroxide solution they suffer tarring.

The cyclization of 2-β-ketoalkylmercaptoimidazoles can be regarded as being an internal alkylation of the imino group in the nucleus of the 2-mercaptoimidazoles by the residue of the carbonyl compound, linked with sulfur; consequently, in the preparation of imidazo-(2,1-b)-thiazoles by the cyclization of 4(5)-phenyl-2-ketoalkylmercaptoimidazoles it is theoretically possible to form two isomers: derivatives of 5-phenylimidazo-(2,1-b)-thiazole and of 6-phenylimidazo-(2,1-b)-thiazole, while for the imidazo-(2,1-b)-tetrahydrobenzothiazole derivative it is theoretically possible to obtain the corresponding 9-phenyl- and 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazoles.



However, in the condensation of 4(5)-phenyl-2-mercaptoimidazole with chloroacetone and with 2-chlorocyclohexanone in hydrochloric acid solution, the same as in the cyclization of the S-acetonyl-, methylacetonyl- and cyclohexanonyl- derivatives of 4(5)-phenyl-2-mercaptoimidazole, into derivatives of imidazo-(2,1-b)-thiazole and of imidazo-(2,1-b)-tetrahydrobenzothiazole, in all cases we were able to isolate but a single isomer. Taking into consideration the fact that only one isomer is formed in the methylation of 4(5)-phenyl-2-benzylmercaptoimidazole, namely: 1-methyl-4-phenyl-2-benzylmercaptoimidazole [7], it could be assumed that the bicyclic compounds obtained by us are derivatives of 6-phenylimidazo-(2,1-b)-thiazole, and the tricyclic—of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole. To prove the structure of these compounds we synthesized them by coincident methods, proceeding from the corresponding 2-aminothiazoles and α-bromoacetophenone.

It is known that 2-aminothiazole and its 4,5-substituted derivatives, the same as other heterocyclic α-amino compounds (2-aminopyridine, 2-aminoquinoline), the amino groups of which form the amidine grouping with nuclear (ring) nitrogen, in the alkylation with alkyl halides form N-alkyl derivatives of thiazoline-2-imides, with alkyls on the nuclear nitrogen atom [8]. The action of α-bromomethyl ketones on 2-aminothiazoles proceeds with the formation of analogous compounds. However, these 3-β-keto derivatives of thiazoline-2-imides were not isolated in the free state, since they easily cleave one molecule of water, being transformed into 6-substituted derivatives of imidazo-(2,1-b)-thiazole [9, 10]. The action of α-halo ketones on 2-aminothiodiazoles gave [11]: 3-phenacyl-, p-nitrophenacyl- and acetonyl- derivatives of thiadiazoline-2-imides.

The boiling in alcohol solution of equimolar amounts of either 2-aminotetrahydrobenzothiazole, 2-amino-4,5-dimethylthiazole or 2-amino-4-methylthiazole with α-bromoacetophenone gave us 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole, 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole and the known 3-methyl-6-phenylimidazo-(2,1-b)-thiazole [9]. These compounds proved to be identical with the substances obtained from 4(5)-phenyl-2-mercaptoimidazole and the corresponding α-halo ketones.

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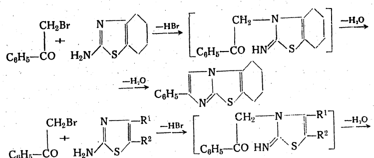

1) $R^1 = CH_3$, $R^2 = H$; 2) $R^1 = R^2 = CH_3$.

As a result, it was elucidated that in the cyclization of 4(5)-phenyl-2- β-ketoalkylmercaptoimidazoles into imidazo-(2,1-b)-thiazoles, the same as in the methylation of 4(5)-phenyl-2-benzylmercaptoimidazole, the phenyl group in the 4 position of the imidazole ring is strengthened [the 6 position in the imidazo-(2,1-b)-thiazole bicycle, and the 10 position in the imidazo-(2,1-b)-tetrahydrobenzothiazole tricycle].

All of the obtained compounds, with the exception of the S-methylacetonyl- and S-cyclohexanonyl derivatives of 4(5)-p-nitrophenyl-2-mercaptoimidazole, were tested in the chemotherapeutical section of the All-Union Scientific-Research Institute of Pharmaceutical Chemistry for antibacterial activity (spectrum of 16 forms of microbes)*. No preparations showing considerable activity were found among these compounds.

EXPERIMENTAL

4(5)-Phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole (III). 10 g of 4(5)-phenyl-2-mercaptoimidazole was added to an alcoholic solution of alkali, prepared from 1.3 g of metallic sodium and 100 ml of 96% ethyl alcohol and the mixture was heated until complete solution of the substance. 7.9 g of 2-chlorocyclohexanone was then added, the solution was heated to 55–60° for 1 hour and 10 minutes at the boiling point of the solvent (until the reaction was neutral on litmus). After separation of the sodium chloride, the solution was cooled. We obtained 10.5 g of compound m.p. 122–123°. The mother liquor was evaporated to low bulk and 4.6 g more of the same compound, m.p. 121–122°, was separated. The total yield of 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole was 15.1 g (97.7%). Colorless spindle-shaped crystals from alcohol, m.p. 123–124°, soluble in most organic solvents, glacial acetic acid and in solutions of mineral acids, difficulty soluble in ether and carbon tetrachloride and insoluble in petroleum ether, water and in alkali solution.

By this method we prepared a series of analogous compounds (see table). If the 2- β-ketoalkly (aryl)-mercaptoimidazole that formed in the reaction was difficultly soluble in alcohol and partically precipitated, after completion of the reaction, the mixture was cooled and the precipitate was filtered off and washed with water to remove the sodium chloride or bromide. Concentration of the alcoholic mother solution yielded somewhat more of the compound. All compounds to be analyzed were recrystallized from ethyl alcohol with the exception of (VIII), which was recrystallized from ethyl acetate.

3-Methyl-6-phenylimidazo-(2,1-b)-thiazole (X). A) 2.75 g of chloroacetone was added to a hot solution of 5 g of 4(5)-phenyl-2-mercaptoimidazole in 80 ml of 36% hydrochloric acid and the mixture was boiled for 1 hour. The light-brown solution was then heated with carbon, filtered and cooled. The white precipitate that formed was filtered off, washed with a small quantity of alcohol and dried. Concentration of the aqueous alcoholic mother liquor to low bulk yielded somewhat more of this substance. Yield 6.5 g (91.5%) of the hydrochloride of 3-methyl-6-phenylimidazo-(2,1-b)-thiazole–colorless needles from alcohol, m.p. 228–232° (with decomp.). Addition of dry sodium bicarbonate to the alcoholic solution of the hydrochloride yielded a base: 3-methyl-6-phenylimidazo-(2,1-b)-thiazole–colorless prisms from alcohol, m.p. 113–113.5°. A test mixture with 3-methyl-6-phenylimidazo-(2,1-b)-thiazole (m.p. 113–113.5°), prepared by condensing 4-methyl-2-aminothiazole with α-bromoacetophenone according to the method of Kondo and Nagasawa [9], melted at 113–113.5°. A test mixture with 4(5)-phenyl-2-acetonylmercaptoimidazole (I) melted at 80–84°.

* The studies were made by S. N. Milovanova and A. A. Mikerina under the supervision of G. N. Pershin.

B) A solution of 1.7 g of the hydrochloride of 4(5)-phenyl-2-acetonylmercaptoimidazole in 30 ml of 38% hydrochloric acid was boiled for 1 hour and then treated as in the previous experiment. Yield 1.5 g (94%) of the hydrochloride of 3-methyl-6-phenylimidazo-(2,1-b)-thiazole, melting range 225–228° (with decomp.) which in sodium bicarbonate solution yielded a base: 3-methyl-6-phenylimidazo-(2,1-b)-thiazole, m.p. 113–113.5°.

C) A solution of 1.3 g of the hydrochloride of 4(5)-phenyl-2-acetonylmercaptoimidazole in 20 ml of n-butyl alcohol was boiled for 1 hour. The precipitate which formed upon cooling was filtered off and dried. Evaporation of the mother liquor to dryness and washing of the crystals with ether yielded somewhat more of this compound. Yield 1.2 g (99%) of the hydrochloride of 3-methyl-6-phenylimidazo-(2, 1-b)-thiazole, melting range (from alcohol) 228–232° (with decomp.). From the hydrochloride we isolated the base–3-methyl-6-phenylimidazo-(2,1-b)-thiazole, m.p. 113–113.5°.

2,3-Dimethyl-6-phenylimidazo-(2,1-b)thiazole (XI). A) A solution of 1 g of 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole in 5 ml of 38% hydrochloric acid was boiled for one hour and then neutralized with sodium carbonate solution. The white precipitate which formed was filtered off, washed with water and dried. Yield 0.9 g (97%) of 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole–colorless flakes, m.p. 157–158° (from alcohol), soluble in ordinary organic solvents, hydrochloric acid, and difficultly soluble in ether and gasoline, insoluble in water and in alkali solution. A test mixture with the initial 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole (m.p. 96–97°) melted at 78- 84°.

Found %: C 68.46: H 5.24; N 11.89; S 14.06. $C_{13}H_{12}N_2S$. Calcd. %: C 68.37; H 5.33; N 12.27; S 14.05.

Hydrochloride–colorless needles from alcohol, m.p. 237–239° (turns brown), soluble in alcohol and in water.

Found %: Cl 13.10. $C_{13}H_{13}N_2ClS$. Calcd. %: Cl 13.40.

B) A solution of 0.6 g of the hydrochloride of 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole in 4 ml of n-butyl alcohol was boiled for 1 hour and then treated as for the preparation of (X) (Method C). Yield 0.55 g (98.2%) of the hydrochloride of 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole, m.p. 237–239° (from alcohol). A test mixture with the hydrochloride of the initial 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole (m.p. 177–178°) melted at 155–158°. Decomposition of the hydrochloride in sodium bicarbonate solution yielded a base–2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole, m.p. 157–158°.

C) A solution of 2.55 g of 4,5-dimethyl-2-aminothiazole [12] and 3.9 g of α-bromoacetophenone in 20 ml of alcohol was boiled for 3 hours. The precipitate which formed upon cooling was filtered off, washed with alcohol, then with ether and dried. Concentration of the mother liquor to low bulk yielded somewhat more of this compound. Yield 6.1 g (92.1%) of the hydrobromide of 2,3-dimethyl-phenylimidazo-(2,1-b)-thiazole, decomposition of which in sodium bicarbonate solution yielded a base: 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole, which after recrystallization from alcohol was in the form of colorless flakes, m.p. 157–158°. A test mixture with the compound, prepared by Method A or B, melted at 157–158°.

10-Phenylimidazo-(2,1-b)tetrahydrobenzothiazol (XII). A) 1 g of 2-chlorocyclohexanone was added to a suspension of 1 g of 4(5)-phenyl-2-mercaptoimidazole in 35 ml of 1% hydrochloric acid and the mixture was boiled for 30 minutes. Activated carbon was then added to the light brown solution and it was boiled for 30 minutes more; the hot solution was then filtered and treated as in the preparation of (XI) (Method A). We obtained 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazol in the form of colorless needles (from alcohol), m.p. 169°, solubility as for (XI). A test mixture with 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole (III) melted at 115–116°.

Found %: C 70.73; H 5.41; N 11.24; S 12.53. $C_{15}H_{14}N_2S$. Calcd. %: C 70.82; H 5.55; N 11.02; S 12.61.

Hydrochloride–colorless flakes (from alcohol), m.p. 273–274° (in a sealed capillary), soluble in water and in alcohol.

Found %: Cl 12.00. $C_{15}H_{15}N_2ClS$. Calcd. %: Cl 12.20.

TABLE

2-β-Ketoalkyl (aryl)-mercaptoimidazoles

Compound No.	R	R′	Yield (in %)	Crystalline form	Melting point	Empirical formula	Molecular weight	Calculated (%) C	Calculated (%) H	Calculated (%) N	Calculated (%) S	Found (%) C	Found (%) H	Found (%) N	Found (%) S
I	H	CH_2COCH_3 *	94.8	Colorless prisms	120—121°	$C_{12}H_{12}ON_2S$	232.16	62.03	5.21	12.07	13.81	61.82	5.15	11.72	13.70
II	H	$CH(CH_3)COCH_3$ **	86.3	Colorless flakes	96—97	$C_{13}H_{14}ON_2S$	246.18	63.37	5.73	11.38	13.03	63.43	5.67	11.19	12.73
III	H	C_6H_9O	97.7	Colorless spindles	123—124	$C_{15}H_{16}ON_2S$	272.20	66.13	5.92	10.29	11.78	65.85	5.77	10.44	12.01
IV	H	$CH_2COC_6H_5$ ***	98.8	Colorless flakes	135—136	$C_{17}H_{14}ON_2S$	294.18	69.34	4.79	9.52	10.90	69.39	4.70	9.30	11.05
V	H	$CH_2COC_6H_4NO_2$-p	96.7	Yellow prisms	155	$C_{17}H_{13}O_3N_3S$	339.18	60.14	3.86	12.39	9.45	59.94	3.84	12.50	9.69
VI	H	$CH_2COC_6H_4NO_2$-m	97.6	Yellow prisms	173—175	$C_{17}H_{13}O_3N_3S$	339.18	60.14	3.86	12.39	9.45	59.96	4.01	12.28	9.27
VII	NO_2	CH_2COCH_3	93.1	Yellow spindles	169.5—170	$C_{12}H_{11}O_3N_3S$	277.17	51.95	4.00	15.16	11.56	51.96	3.91	15.48	11.51
VIII	NO_2	$CH(CH_3)COCH_3$	90.0	Yellow spindles	130—132	$C_{13}H_{13}O_3N_3S$	291.18	53.57	4.49	14.43	11.01	53.35	4.43	14.08	10.98
IX	NO_2	C_6H_9O	95.1	Yellow spindles	182—183	$C_{15}H_{15}O_3N_3S$	317.20	56.74	4.76	13.25	10.10	56.67	4.81	13.24	9.86

* Hydrochloride—colorless flakes from alcohol, m.p. 153°. Found %: Cl 13.27. $C_{12}H_{13}ON_2ClS$. Calcd. %: Cl 13.22. Semicarbazone—colorless crystals from alcohol, m.p. 146–148°. Found %: N 23.94. $C_{13}H_{15}ON_5S$. Calcd. %: N 24.22.

** Hydrochloride—colorless flakes from alcohol, m.p. 177–178° (with decomp.). Found %: Cl 12.40. $C_{13}H_{15}ON_2ClS$. Calcd. %: Cl 12.54.

*** Hydrochloride—colorless flakes from alcohol, m.p. 220–222° (with decomp.). Found %: Cl 10.75. $C_{17}H_{15}ON_2ClS$. Calcd. %: Cl 10.72. Hydrobromide—colorless threadlike crystals, m.p. 226–227° (with decomp.). Found %: Br 21.63. $C_{17}H_{15}ON_2BrS$. Calcd. %: Br 21.30. Semicarbazone—colorless crystals from alcohol, m.p. 179–181°. Found %: N 20.17. $C_{18}H_{17}ON_5S$. Calcd. %: N 19.94.

B) A solution of 0.8 g of 4(5)-phenyl-2-(2′-cyclohexanonyl)-mercaptoimidazole in 8 ml of 38% hydrochloric acid was boiled for 1 hour and then treated as in the previous experiment. Yield 0.72 g (97.3%) of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole, m.p. 168–169° which after recrystallization from alcohol was in the form of colorless needles, m.p. 169°.

C) A solution 0.59 g of 2-amino-4,5,6,7-tetrahydrobenzothiazole [13] and 0.75 g of α-bromoacetophenone in 10 ml of alcohol was boiled for 3 hours. After cooling, ether was added to the colorless solution and the precipitate that formed (hydrobromide of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole (1.2 g, 90 %) was filtered off, washed with ether and decomposed in sodium bicarbonate solution. We obtained 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole in the form of colorless needles from alcohol, m.p. 169°. A test mixture with the compound, prepared by Method A or B, melted at 169°.

SUMMARY

1. The reactions of 4(5)-phenyl- and 4(5)-p-nitrophenyl-2-mercaptoimidazoles with α-halo ketones of the fatty, fatty-aromatic and alicyclic series gave 2-β-ketoalkyl (aryl)-mercaptoimidazoles.

2. The reaction of 4(5)-phenyl-2-mercaptoimidazole with α-halo ketones of either the fatty or alicyclic series in hydrochloric acid solution, or under boiling of the corresponding 4(5)-phenyl-2-β-ketoalkylmercaptoimidazoles in hydrochloric acid, gave substituted imidazo-(2,1-b)-thiazole and imidazo-(2,1-b)-tetrahydrobenzothiazole derivatives. The structure of these compounds was established by their coincident synthesis from the corresponding 2-aminothiazoles.

3. The catalytic influence of hydrogen ions for the closure of the thiazole ring in the cyclizations of 4(5)-phenyl-2-β-ketoalkylmercaptoimidazoles into imidazo-(2,1-b)-thiazoles was shown.

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AMINOACRIQUINE AND ITS ANALOGS

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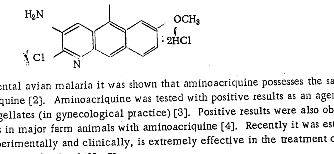
A large number of acridine derivatives are characterized by diverse biological acitivity (antiviral, bactericidal, antimalarial, antihelminthic, etc.); in this connection only a few acridine compounds, showing high activity, possess relatively low toxicity. Such compounds have found use as medicinal agents (acriquine, rivanol, trypaflavin, etc.).

A compound synthesized in the USSR with a structure close to that of acriquine is aminoacriquine: 2-methoxy-6-chloro-7-amino-9-(1-diethylamino-4-methylbutyl)-aminoacridine dihydrochloride [1], which shows highly diverse biological activity.



In experimental avian malaria it was shown that aminoacriquine possesses the same activity and is less toxic than acriquine [2]. Aminoacriquine was tested with positive results as an agent for the treatment of trichomonad flagellates (in gynecological practice) [3]. Positive results were also obtained in the treatment of theileriosis in major farm animals with aminoacriquine [4]. Recently it was established that aminoacriquine, both experimentally and clinically, is extremely effective in the treatment of various vermicular diseases in both humans and animals [5–7].

Acriquine analogs close to aminoacriquine in structure, not substituted in position 7, containing the substituents OCH_3 and Cl in the 2 and 6 positions of the acridine ring, and a dialkylaminoaklylamine residue in the 9 position, have been synthesized in extremely large number and have been tested, in comparison to acriquine, for their antimalarial activity [8, 9]. Similar aminoacriquine analogs, containing the NH_2-group as additional substituent in the 7 position of the acridine ring, up to now have remained unknown and have not been tested for their biological activity.

In this communication we describe a number of such compounds, more readily available than aminoacriquine itself. We synthesized these compounds for the purpose of studying their biological activity, in comparison to aminoacriquine. The 2-methoxy-7-nitro-6,9-dichloroacridine needed for the synthesis of aminoacriquine and its analogs was obtained by the method described earlier [10]. This compound cannot be obtained from 2-methoxy-6,9-dichloroacridine, an intermediate in the production of acriquine, by its nitration, since the mixture of nitro compounds obtained here predominantly contains the nitromethoxydichloroacridine in which the nitro group is found in other than the 7 position. For the most part the necessary diamines were prepared without difficulty by known procedures.

An attempt was made by us to improve the synthesis of 1-dialkylamino-3-aminobutanes from the readily accessible 1,3-dialkylaminoketones [11]. The catalytic reductive amination of 1,4-dialkylaminoketones leads to varying yields of 1,4-diamines. However, in the case of the 1,3-dialkylaminoketones, with this method we were able to obtain the 1,3-diamines only in insignificant yield, since here most of the substance suffered cleavage with the formation of dialkylamine and 2-butanol. This agrees with other similar observations made on the behavior of 1,3-aminoketones in reduction reactions [12]. The synthesis of the 1,3-diamines is best realized through the aminoketone oximes, and in this connection the catalytic reduction of the oximes fails to give a better yield of the diamine than when sodium in alcohol is used for the reduction [13].

To obtain the 1-diethylamino-4-aminobutane it proved most expedient to reduce the corrosponding diethylaminobutyronitrile with hydrogen in the presence of nickel catalyst.

The condensation of the diamines with 2-methoxy-7-nitro-6,9-dichloroacridine was run in phenol medium by the generally accepted method [1, 10, 13]. The nitro compounds were reduced with stannous chloride in aqueous-alcohol hydrochloric acid [1, 14]. Catalytic reduction with hydrogen in the presence of nickel can also be successfully used here. We used the latter method to prepare large amounts of aminoacriquine for an extensive study of its practical applications. The reduction is run at low temperature, since under these conditions the chlorine contained in the substituted nitroacridine molecule remains intact.

Aminoacriquine and its analogs favorably differ from related compounds, not having the amino group as substituent in the 7 position, in that their hydrochlorides are more stable in water solutions, while biologically they show lower toxicity. This possesses essential importance for the preparation and practical utilization of these compounds.

High antimalarial activity was shown experimentally (data of A. V. Stoyanova) by the aminoacriquine analogs—the dihydrochlorides of 2-methoxy-6-chloro-7-amino-9-(1-diethylamino-2-hydroxypropyl)-aminoacridine and of 2-methoxy-6-chloro-7-amino-9-(1-diethylaminobutyl)-aminoacridine. The chemotherapeutic index for the last compound was determined to be 2.8, while for aminoacriquine it is 1.78; the index for acriquine is equal to 1.0. Making the aminoacriquine molecule either simpler or more complex, on the basis of changes made in other than the 9 position, leads to loss in antimalarial activity. Our synthesized 2-amino-9-(1-diethylamino-4-methylbutyl)-aminoacridine and 2,3-dimethoxy-6-chloro-7-amino-9-(1-diethylamino-4-methylbutyl)-aminoacridine proved to be inactive in the experimental treatment of avian malaria (A. V. Stoyanova).

EXPERIMENTAL

Nitration of 2-methoxy-6,9-dichloracridine. A mixture of 3 ml of nitric acid (d 1.5) and 6 ml of sulfuric acid was added to a solution of 20 g of 2-methoxy-6,9-dichloracridine (m.p. 160–161°) [13] in 120 ml of concentrated sulfuric acid at 25°. The mixture was stirred for 1.5 hours at 50° and after cooling, was poured on ice and neutralized with ammonia solution. The washed, dried nitration product (23 g) was dissolved with heating in 800 ml of dichloroethane. Upon cooling, 9 g of crystals (m.p. 225–228°) came down; a second crystallization from dichloroethane yielded 6.4 g (27%) of nitromethoxydichloroacridine crystals. Yellow needles, m.p. 241–242° [10]; m.p. 272–273° for 4-nitro isomer [14].

Found %: N 8.55; Cl 21.88. $C_{14}H_8O_3N_2Cl_2$. Calcd. %: N 8.65; Cl 21.91.

Diamines

The following dialkylaminoaklylamines were prepared: 1,2-diethylaminoaminoethane from ethanolamine [13]; 1,3-diethylaminoaminopropane from diethylaminopropyl chloride [13]; 1-diethylamino-2-hydroxy-3-aminopropane from ethylene chlorohydrin [15]; 1-diethylamino-4-aminobutane by catalytic reduction of diethylaminobutyronitrile; 1-dimethylamino-3-aminobutane by reduction of oxime of dimethylaminobutanone. 1,4-Diethylaminoaminopentane was obtained from preparation of acriquine.

1-Dimethylamino-3-aminobutane. The oxime of the aminoketone was prepared by the method given previously for the diethylamino compound [13]; the oxime was a viscous, colorless liquid, b.p. 136–137° (38–40 mm). A solution of 35 g of the oxime in 100 ml of absolute ethyl acetate was reduced with hydrogen in an autoclave at 70–85° in presence of 6 g skeletal nickel catalyst. The initial hydrogen pressure was 15 atm. From a solution in ethyl acetate, the diamine was extracted with 10% acetic acid; the solution of the diamine salt was evaporated down, the diamine was separated with solid alkali, dried by it and distilled. We collected 16 g (49.2%) of the fraction which boiled at 132–137° and contained 96.6% of diamine (d_{20} 0.8122, n_D^{20} 1.4322).

1-Diethylamino-4-aminobutane. 166 g of γ-diethylaminobutyronitrile [16], b.p. 93–94° (13 mm), 410 ml of 12% ammonia solution and 15 g of a slurry of skeletel Ni catalyst were placed in an autoclave. The autoclave was filled with hydrogen until the pressure was 20 atm. The hydrogen was vigorously absorbed upon stirring at 90–105°. From time to time additional hydrogen was fed in. After absorption of hydrogen ceased, the reaction solution was cooled and filtered free of catalyst and the diamine was separated from the filtrate by dissolving solid caustic soda in the filtrate. The remaining diamine was steam-distilled from the

alkaline solution. The alkali-dried diamine was vacuum-distilled. Yield 135 g (80%) of 1-diethylamino-4-aminobutane, boiling range 89-93° (27 mm) which was the main fraction. By acidometric titration with methyl red as an indicator the content of 1-deithylamino-4-aminobutane in this fraction was determined to be 98.9%.

2-Methoxy-6-chloro-7-nitroacridines with various substituents in the 9 position, were prepared by means of a general method: 2-methoxy-7-nitro-6,9-dichloracridine was heated with the diamine (small excess) in a phenolic medium at 100° for 2 hours. The reaction mass was then poured into a 10% alkali solution; the nitroacridine base was washed with 2% alkali solution, with water, and crystallized from the solvent, (mainly, from dry acetone) (in certain cases water was added to the resulting solution).

2-Methoxy-6-chloro-7-nitro-9-aminoacridine was prepared by the method that A. Albert recommended for the preparation of 9-aminoacridine [17.].

The prepared nitroacridines are described in Table 1, which shows that as the number of carbon atoms in the "chain" increases at position 9, the melting point of the compound falls, the solubility in acetone

TABLE 1

9-Substituted 2-Methoxy-6-chloro-7-nitroacridines of General Formula

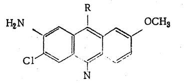
Substituents	General formula	Analysis (in %) calculated N	found N	Properties
9-Amino-,	$C_{14}H_{10}O_3N_3Cl$	13.83	13.71	Red crystals from nitrobenzene (1:200), m.p. 298-300°
9-β-Diethylaminoethylamino-,	$C_{20}H_{23}O_3N_4Cl$	13.91	14.20	Bright red crystals from acetone (1:75), m.p. 187-188°
9-γ-Diethylaminopropylamino-,	$C_{21}H_{25}O_3N_4Cl$	13.4	13.27	Dark red needles from acetone (1:20), m.p. 150-151°
9-γ-Diethylamino-β-hydroxy-propylamino-,	$C_{21}H_{25}O_4N_4Cl$	12.9	13.0	Red crystals from acetone (1:20), m.p. 145-146°
9-γ-Dimethylamino-α-methyl-propylamino-,	$C_{20}H_{23}O_3N_4Cl \cdot H_2O$	13.3, H_2O 4.28	12.91, H_2O 4.49	Fine red crystals from acetone (1:5), m.p. 135-136°
9-δ-Diethylaminobutylamino-,	$C_{22}H_{27}O_3N_4CL \cdot H_2O$	12.6, H_2O 4.0	12.59, H_2O 4.8	Dark red needles from acetone (1:25), m.p. 133-134°

increases and the formation of crystals becomes more difficult. The described nitroacridines form salts with acids that are soluble in water. Even upon brief boiling of the aqueous solutions of the hydrochlorides of substituted 7-nitroacridines, hydrolysis takes place and 2-methoxy-6-chloro-7-nitroacridine precipitates out.

2-Methoxy-6-chloro-7-aminoacridines with various substituents in the 9 position were prepared from nitro compounds described in Table 1 by reduction with stannous chloride and slight modifications of the prescription given for the preparation of aminoacriquine [1]. The commerical aminoacriquine base, this time, immediately dissolved in acetone and from the filtered solution the hydrochloride was obtained by acidification with a mixture (1:9) of concentrated hydrochloric acid and acetone. For characterization of the base, it was obtained from the aqueous solution of the salt by addition of caustic soda solution. The prepared compounds are described in Table 2.

TABLE 2

9-Substituted 2-Methoxy-6-chloro-7-aminoacridines of General Formula



Substituents	General formula	Analysis (in %) calculated	Analysis (in %) found	Properties
9-Amino-	$C_{14}H_{12}ON_3Cl$	Cl 12.86	Cl 12.89	Yellow-brown powder from $CH_3OH + H_2O$, m.p. 250-252°
Dihydrochloride	$C_{14}H_{12}ON_3Cl \cdot 2HCl$	N 10.91	N 10.84	Yellow-orange powder, m.p. 304-306° (decomp.)
9-β-Diethylaminoethylamino-	$C_{20}H_{25}ON_4Cl$	N 15.0	N 14.8	Golden scales from acetone-water mixture, m.p. 190-191°
Dihydrochloride	$C_{20}H_{25}ON_4Cl \cdot 2HCl$	Cl' 15.9	Cl' 15.45	Orange-yellow powder, m.p. 240-242° (decomp.)
9-γ-Diethylaminopropyl-amino-	$C_{21}H_{27}ON_4Cl$	N 14.48	N 14.41	Yellow-green powder, m.p. 145-146°
Dihydrochloride	$C_{21}H_{27}ON_4Cl \cdot 2HCl \cdot 2H_2O$	Cl' 14.3, H_2O 7.26	Cl' 14.15, H_2O 8.07	Orange powder, m.p. 280-282° (decomp.)
9-γ-Diethylamino-β-hydroxy-propylamino-	$C_{21}H_{27}O_2N_4Cl$	N 13.9	N 13.75	Yellow-green, fine crystalline powder, m.p. 136-137°
Dihydrochloride	$C_{21}H_{27}O_2N_4Cl \cdot 2HCl \cdot 3H_2O$	Cl' 13.18, H_2O 10.18	Cl' 12.85, H_2O 10.63	Orange powder, m.p. 272-274° (decomp.)
9-γ-Dimethylamino-α-methyl-propylamino-	$C_{20}H_{25}ON_4Cl$	N 15.0	N 15.05	Yellow powder, m.p. 160-162°
Dihydrochloride	$C_{20}H_{25}ON_4Cl \cdot 2HCl \cdot 3H_2O$	Cl' 14.02, H_2O 10.0	Cl' 14.15, H_2O 9.16	Orange powder, m.p. 272-274°
9-δ-Diethylaminobutylamino-	$C_{22}H_{29}ON_4Cl$	N 13.97	N 13.99	Yellow crystals, m.p. 118.5-119.5°
Dihydrochloride	$C_{22}H_{29}ON_4Cl \cdot 2HCl \cdot H_2O$	N 11.38, H_2O 3.66	N 11.20, H_2O 3.49	Orange-yellow needles, m.p. 268-270° (decomp.)

The hydrochlorides of the aminoacriquine analogs were readily soluble in hot water; in cold water they were soluble in the ratio 1:60-1:100 parts, i.e., slightly less than acriquine and aminoacriquine (1:30). Aqueous solutions of aminoacriquine and its analogs remained transparent upon being heated (100°) for several hours; under these conditions, consequently, the compounds did not hydrolyze.

2-Amino-9-(1-diethylamino-4-methylbutyl)-aminoacridine. The reaction of 2-nitro-9-chloroacridine and 1-diethylamino-4-aminopentane in phenolic medium yielded 2-nitro-9-δ-diethylamino-α-methylbutyl-aminoacridine as bright red cubes from ether, m.p. 80-81°.

Found %: N 14.07; H_2O 4.2. $C_{22}H_{28}O_2N_4 \cdot H_2O$. Calcd. %: N 14.06; H_2O 4.5.

Reduction of the nitro compound yielded 2-amino-9-(1-diethylamino-4-methylbutyl)-aminoacridine, which was isolated as the hydrochloride, a yellow powder which was readily soluble in water, m.p. 165-168°.

Found %: Cl' 16.74 (potentiometrically). $C_{22}H_{30}N_4 \cdot 2HCl$. Calcd. %: Cl' 16.77.

2,3-Dimethoxy-6-chloro-7-amino-9-(1-diethylamino-4-methylbutyl)-aminoacridine. * 3',4'-Dimethoxy-4-nitro-5-chlorodiphenylamine-2-carboxylic acid was prepared by the general scheme from 2,4-dichloro-5-nitro-benzoic acid and 4-aminoveratrole. The acid was in the form of dark yellow needles from alcohol, m.p. 240-242°.

* Carried out with the participation of S. S. Kogan.

Found %: N 7.78. $C_{15}H_{13}O_6N_2Cl$. Calcd. %: C 7.94.

2,3-Dimethoxy -6-chloro-7-nitro-9-chloroacridine. It was prepared from the preceding acid and phosphorus oxychloride in the same manner as other similar compounds; yellow-green needles from dichloro-ethane, m.p. 240-241°.

Found %: N 7.81. $C_{15}H_{10}O_4N_2Cl_2$. Calcd. %: N 7.93.

2,3-Dimethoxy-6-chloro-7-nitro-9-(1-diethylamino-4-methylbutyl)-aminoacridine. It was synthesized from the preceding dichloroacridine and 1-diethylamino-4-aminopentane. Orange-red crystals from acetone, m.p. 94-95°

Found %: N 11.72. $C_{24}H_{31}O_4N_4Cl$. Calcd. %: N 11.79.

2,3-Dimethoxy-6- chloro -7-amino-9-(1-diethylamino-4-methylbutyl)-aminoacridine. It was prepared in the same manner as the other related compounds. The substance was isolated in the form of the orange hydrochloride, readily soluble in water, m.p. 130-132°.

Found %: N 10.81. $C_{24}H_{33}O_2N_4Cl \cdot 2HCl$. Calcd. %: N 10.86.

Aminoacriquine *

2.5 liters acetone, 500 g 2-methoxy-6-chloro-7-nitro-9-(1-diethylamino-4-methylbutyl)-amino-acridine (base of 7-nitroacriquine [1]) and 125 g skeletal Ni catalyst in the form of a slurry were placed in an enameled autoclave. The air was removed from the autoclave with nitrogen or hydrogen. Hydrogenation was carried out at a temperature of 22-26°. The introduction of hydrogen was from a cylinder at a pressure of up to 1 atm. The absorption of hydrogen (80-82 liters) was continued for 12-15 hours. The completion of the reaction was judged by decrease in the hydrogen absorption. The reaction mass was filtered and the filtrate was transfered to an enameled boiler, externally cooled with ice water. When the temperature of the mass reached 4-5°, a mixture of concentrated hydrochloric acid and acetone (1:9) was added through a dropping funnel with stirring until the pH was 6.0. 1300 ml of the above mixture was consumed.

Aminoacriquine was isolated in the form of orange-red crystals which were washed with acetone (500 ml). The compound was dried first at room temperature and then at 60-80°. Yield of aminoacridine $C_{23}H_{31}ON_4Cl \cdot 2HCl$** 460 g (84%), m.p. 259-260° (decomp.).

The allowable moisture content of aminoacriquine that is prepared for practical use is 8%. Below are given the analytical data of separate series of synthesized aminoacriquine preparations.

Found (recalculated on dry substance) %: N 11.3-11.5; Cl' 14.3-14.5; Cl (total) 21.4-21.9. $C_{23}H_{31}ON_4Cl \cdot 2HCl$. Calcd. %: N 11.48; Cl' 14.54; Cl (total) 21.8.

SUMMARY

1. The properties shown by aminoacriquine and its analogs permit considering this series of acridine derivatives as possessing great interest relative to studying their inherent biological activity.

2. A number of new acridine derivatives, analogs of aminoacriquine, have been described. These new compounds were synthesized for the purpose of studying their biological activity, in comparison to amino-acriquine.

3. In the last step for the synthesis of aminoacriquine and its analogs it is expedient to realize the catalytic reduction of the preceding nitro compounds with hydrogen in the presence of nickel, under mild conditions, where dehalogenation of the nitrochloroacridine cannot occur.

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* A. T. Chernyaeva and P. I. Filimonov participated.

** When the formula of aminoacriquine [1] was first determined only on the basis of nitrogen determination, it was erroneously given as: $C_{23}H_{31}O_4NCl \cdot 3HCl$.

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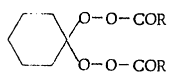
Part 2

IN ENGLISH TRANSLATION

OXIDATIVE ACTION OF SOME ACYL PEROXIDES

G. A. Razuvaev, L. V. Stupen and K. S. Minsker

Recently a paper was published by Cooper [1] on the synthesis of peroxides from hydroxycyclohexyl hydroperoxide and acid chlorides, for which the author gives the formulas:



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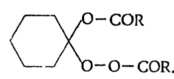

(II)

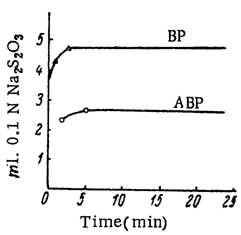

Fig. 1. Oxidative action of benzoyl (BP) and acetylbenzoyl (ABP) peroxides.

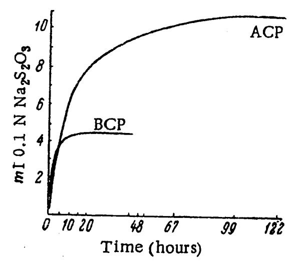

Fig. 2. Oxidative action of hydroxycyclohexyl hydroperoxide derivatives. BCP—benzoyl derivative; ACP— acetyl derivative.

On the basis of the high amount of iodine evolved from HI the author expresses himself in favor of formula (I). Working with peroxides, we also analyzed them iodometrically. We prepared two peroxides—the acetyl derivative (ACP), with m.p. 71°, and the benzoyl derivative (BCP), with m.p. 80-80.5°. The peroxides were obtained by the Cooper method from twice recrystallized hydroperoxide with m.p. 79°. The determination made by us showed for BCP ($R = C_6H_5$), a 70.3% content of Form (I), but for ACP ($R = CH_3$) the amount of peroxide (I) found was equal to 99.3%.

In the iodometric determinations the exceedingly slow iodine liberation drew our interest. Operating in dichloroethane solution containing acetic acid, we compared the oxidative action of the peroxides ACP and BCP, and also of benzoyl (BP) and acetylbenzoyl (ABP) peroxides, the latter having m.p. 38°, on the reaction for the liberation of iodine from KI. For the last two peroxides the iodine liberation is completed in several minutes (Fig. 1), while with ACP and BCP a considerably longer time is required (Fig. 2). For these peroxides the iodine liberation rate can be satisfactorily expressed by the equation: $y = \frac{x}{a + bx}$, where y is the number of milliliters of 0.1 N $Na_2S_2O_3$ solution required for the titration; x is the time of titration in minutes from the start of the reaction; and a and b are coefficients, different for ACP and BCP (for ACP at 22° a was found to be equal to 49.2, and b was found to be equal to 0.0857).

It is interesting to mention that despite the great difference in the rates of iodine liberation from KI, the peroxides ACP and BCP are powerful initiators for the polymerization of styrene [1]: they concede nothing to either BP or ABP in their strength of action.

The difference in the rates of the oxidation and polymerization reactions should be explained as being due to a difference in their mechanism: the rate of the polymerization reaction is determined by the decomposition rate of the peroxides into radicals, while the oxidative action proceeds through an ionic mechanism.

EXPERIMENTAL

The recrystallized peroxide was dissolved in twice distilled dichloroethane. 10 ml of the peroxide solution, 3.5 ml chemically pure glacial acetic acid and 11 ml of 5% KI solution in methanol were placed in a flask with a ground stopper. The methanol had been previously treated with activated charcoal and twice distilled. The mixture was kept in the dark and the iodine which formed was titrated with 0.1 N hyposulfite solution. Control samples were worked side by side.

The analytical data are given in the table.

TABLE

Investigated compound	Peroxide (in g)	Solvent (in g)	Time attaining equilibrium	Found peroxide (in %)
BP	2.250	447.77	3 min.	99.4
ABP	1.762	398.09	5 min.	99.0
ACP	4.310	1470.00	99 hrs.	99.3 *
BCP	2.150	429.70	22 hrs.	70.3*

SUMMARY

1. The oxidative action of BP, ABP, BCP and ACP on the rate of iodine liberation from KI was investigated. It was established that an exceedingly great difference exists in the oxidation rates of BP and ABP (3-5 minutes) and of BCP and ACP (20-100 hours).

2. A mathematical equation was given to express the oxidation rate when BCP and ACP are used.

3. The initiating action rate is completely independent of the oxidative action rate, which is explained by a different mechanism for the two processes.

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Received July 10, 1955

* Recalculated on basis of Formula (I).

SYNTHESIS AND POLYMERIZATION OF THIOESTERS OF METHACRYLIC ACID

M. M. Koton, T. M. Kiseleva and K. S. Podgorskaya

Of the great number of acrylic and methacrylic acid derivatives that have been studied, there is hardly any information on the sulfur containing derivatives of these acids. Only the thiodiglycol ester of dimethylacrylic acid has been described [1], and very brief mention [2] has also been made of the synthesis of acrylic acid thioesters as colorless liquids with unpleasant odor, and a strong tendency for polymerization. We were the first to synthesize the thioesters of methacrylic acid, starting from benzyl mercaptan and thiophenol. The thioesters of methacrylic acid polymerize with great ease, even when stored at temperatures below 0°, to yield brittle colorless polymers with a disagreeable odor.

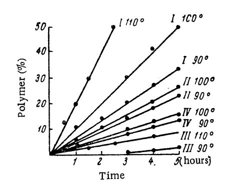

Fig. 1. Polymerization of methacrylic acid esters.

I) Benzyl ester; II) thiobenzyl ester; III) phenyl ester; IV) thiophenyl ester.

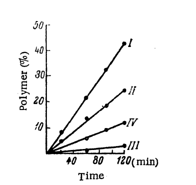

Fig. 2. Polymerization of methacrylic acid esters at 70° in the presence of 0.1% benzoyl peroxide.

I) Benzyl ester; II) thiobenzyl ester; III) phenyl ester; IV) thiophenyl ester.

It seemed of interest to us to study the effect on the polymerization tendency of replacing the oxygen atom in the phenyl and benzyl esters of methacrylic acid by the sulfur atom. For this purpose we studied the polymerization of the four methacrylic acid esters:

$$CH_2{=}C(CH_3)CO{-}O{-}CH_2C_6H_5 \quad (I), \qquad CH_2{=}C(CH_3)CO{-}S{-}CH_2C_6H_5 \quad (II),$$

$$CH_2{=}C(CH_3)CO{-}O{-}C_6H_5 \quad (III), \qquad CH_2{=}C(CH_3)CO{-}S{-}C_6H_5 \quad (IV)$$

at 90, 100 and 110° in the absence of initiators (Fig. 1), and at 70° in the presence of 0.1% benzoyl peroxide (Fig. 2). From Figs. 1 and 2 it follows that the benzyl and thiobenzyl esters of methacrylic acid polymerize with considerably greater ease than do the corresponding phenyl and thiophenyl esters; here benzyl methacrylate (I) polymerizes at a rate 1.5 times that shown by thiobenzyl methacrylate (II).

A comparison of the phenyl and thiophenyl esters of methacrylic acid shows that in this case the replacement of the oxygen atom by sulfur leads to considerable enhancement in the polymerization ability; on the average the thiophenyl methacrylate polymerizes 5 times more rapidly than does phenyl methacrylate (III).

A study of the intrinsic viscosities [η] of the polymers shows that the phenyl methacrylate polymers possess the highest [η] value, and the thiobenzyl methacrylate polymers the lowest (cf. table).

EXPERIMENTAL

Thiophenyl methacrylate was prepared by reacting thiophenol with methacrylyl chloride in alkaline solution as per equation:

$$CH_2{=}C(CH_3)COCl + C_6H_5SH + NaOH \rightarrow CH_2{=}C(CH_3)CO{-}S{-}C_6H_5 + NaCl + H_2O.$$

10 g of thiophenol was dissolved in 100 ml of 5% caustic soda solution. 10.5 g of methacrylyl chloride was then added in the course of 30 minutes, drop-wise, with stirring and cooling (in ice) and the liquid was stirred for 1 hour more at room temperature. The reaction mass was extracted with ether, the ethereal solution was washed with water until neutral reaction was obtained and then dried over anhydrous magnesium sulfate. After removal of ether, the residue was vacuum-distilled. Yield 8 g (56%) of thiophenyl methacrylate; a colorless transparent liquid with an unpleasant odor, b.p. 106-107° at 4 mm, 117° at 8 mm, n_D^{18} 1.5785, n_D^{20} 1.5774.

Found %: S 17.68. $C_{10}H_{10}OS$. Calcd. %: S 17.98.

Phenyl methacrylate was synthesized similarly from methacrylyl chloride and phenol [3] in the form of colorless liquid, b.p. 80-82° at 4 mm, n_D^{20} 1.5163 (n_D^{20} 1.5156 [3]).

Name	[η] 100°	[η] 110°
Benzyl methacrylate	1.31	0.96
Thiobenzyl methacrylate	0.14	0.13
Thiophenyl methacrylate	1.46	1.42
Phenyl methacrylate	–	1.80

Thiobenzyl methacrylate was prepared similarly to thiophenyl methacrylate. 10.5 g of methacrylyl chloride was added to 12.5 g of benzylmercaptan, dissolved in 100 ml of 5% caustic soda solution and treatment was carried out as above. Yield 9.8 g (48%). Thiobenzyl methacrylate was a colorless transparent liquid with an unpleasant odor, b.p. 119-120° at 4 mm, 130° at 6 mm, n_D^{20} 1.5681.

Found %: S 16.73. $C_{11}H_{12}OS$. Calcd. %: S 16.67.

Benzyl methacrylate [3] was prepared similarly from benzyl alcohol and methacrylyl chloride; it was a colorless liquid, b.p. 104-106° at 6 mm, n_D^{20} 1.5143 (1.5140 [3]).

A study of the polymerization of the above esters of methacrylic acid was carried out in sealed glass ampoules, heated in an oil thermostat with precise regulation of temperature ±0.2°. The monomers which were placed in ampoules were subjected to multiple freezings in dry ice and vacuum treatment in order to remove atmospheric oxygen. The yield of polymers was determined by a method involving precipitation with methanol from chloroform solutions.

SUMMARY

1. The previously unknown phenyl and benzyl thioesters of methacrylic acid were synthesized.

2. It was shown that the phenyl and benzyl thioesters of methacrylic acid are easily polymerized, both in the presence of benzoyl peroxide and in the absence of initiators.

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[1] Monomers, Symposium No 2, 68 (1953).

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HETEROCYCLIC COMPOUNDS

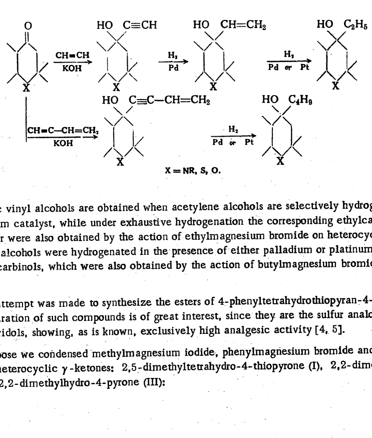
35. CONDENSATION OF TETRAHYDRO-γ-PYRONES AND TETRAHYDRO-γ-THIOPYRONES WITH ORGANOMAGNESIUM AND-LITHIUM COMPOUNDS

I. N. Nazarov and E. T. Golovin

As is known, γ-piperidones are easily reduced to secondary γ-piperidols [1-3], but react very poorly as Grignard reagents (alkylmagnesium halides and arylmagnesium halides) and in this connection give the corresponding tertiary γ-piperidols only in very low yields. In order to run this reaction with satisfactory results it is necessary to use organolithium compounds, as was shown in previous papers from our laboratory and by other investigators [4, 5].

All of the tetrahydro-γ-thiopyranols known up to now have been obtained from tetrahydro-γ-thiopyrones, either by reduction with aluminum isopropylate [6] or by condensation with Grignard reagents [6-9]. Tetrahydro-γ-pyranol has also been obtained by the hydrogenation of γ-pyrone on Raney nickel catalyst [6].

It was communicated earlier that γ-piperidones, tetrahydro-γ-thiopyrones and tetrahydro-γ-pyrones in the presence of pulverized potassium hydroxide condense with acetylene and with vinylacetylene, giving the corresponding heterocyclic acetylene and vinylacetylene alcohols in high yields [7, 10-12].

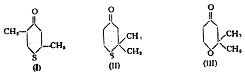


X = NR, S, O.

Heterocyclic vinyl alcohols are obtained when acetylene alcohols are selectively hydrogenated in the presence of palladium catalyst, while under exhaustive hydrogenation the corresponding ethylcarbinols were obtained. The latter were also obtained by the action of ethylmagnesium bromide on heterocyclic γ-ketones. The vinylacetylene alcohols were hydrogenated in the presence of either palladium or platinum catalyst to the corresponding butylcarbinols, which were also obtained by the action of butylmagnesium bromide on heterocyclic γ-ketones.

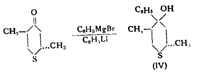
In 1950 an attempt was made to synthesize the esters of 4-phenyltetrahydrothiopyran-4-ol [13]. Without doubt, the preparation of such compounds is of great interest, since they are the sulfur analogs of the esters of 4-phenyl-4-piperidols, showing, as is known, exclusively high analgesic activity [4, 5].

For this purpose we condensed methylmagnesium iodide, phenylmagnesium bromide and phenyllithium with the following heterocyclic γ-ketones: 2,5-dimethyltetrahydro-4-thiopyrone (I), 2,2-dimethyltetrahydro-4-thiopyrone (II) and 2,2-dimethylhydro-4-pyrone (III):



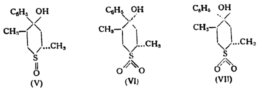
(I) (II) (III)

The reaction of 2,5-dimethyltetrahydro-4-thiopyrone (I) (trans-isomer) with phenylmagnesium bromide gave 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV) in 41% yield, which was also obtained in 65% yield by the action of phenyllithium on ketone (I).



(IV)

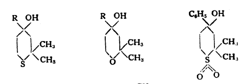
The oxidation of the obtained phenylthiopyranol (IV) with potassium permanganate in acetone solution in the presence of 10% sulfuric acid gave the corresponding sulfoxide (V) and two sulfone diastereoisomers of the trans- series (VI) and (VII):



(V) (VI) (VII)

As a result, the action of either phenylmagnesium bromide or of phenyllithium on trans-2,5-dimethyltetrahydro-4-thiopyrone (I) gives a mixture of both stereoisomeric trans-2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ols, which we were able to separate as their crystalline sulfones (VI) and (VII).

The action of either methylmagnesium iodide or of phenylmagnesium bromide on 2,2-dimethyltetrahydro-4-thiopyrone (II) and 2,2-dimethyltetrahydro-4-pyrone (III) respectively, gave 2,2,4-trimethyltetrahydrothiopyran-4-ol (VIII) (60% yield), 2,2-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IX) (68% yield), 2,2,4-trimethyltetrahydropyran-4-ol (X) (64% yield) and 2,2-dimethyl-4-phenyltetrahydropyran-4-ol (XI) (76% yield):



(VIII) $R = CH_3$
(IX) $R = C_6H_5$

(X) $R = CH_3$
(XI) $R = C_6H_5$

(XII)

2,2-Dimethyl-4-phenyltetrahydrothiopyran-4-ol (IX) was quantitatively converted into the sulfone (XII) by oxidation with potassium permanganate in acetone solution in the presence of 10% sulfuric acid.

In all cases the organomagnesium compound was taken in 20% excess of the amount required by theory.

It should be mentioned that of the heterocyclic γ-ketones taken for reaction the least reactive with respect to organometallic compounds proved to be 2,5-dimethyltetrahydro-4-thiopyrone (I). As can be seen from the experimental data, in its condensation with phenylmagnesium bromide a prolonged boiling (15-20 hours)

of the reaction mixture is required to achieve a 40% yield of the corresponding alcohol, and even with phenyllithium the yield of the phenylthiopyranol (IV) fails to exceed 65%. At the same time its 2,2-dimethyl-substituted isomer (II) reacts with phenylmagnesium bromide, under 2-hour boiling of the reaction mixture, to give the corresponding alcohol in 68% yield, while the 2,2-dimethyltetrahydro-4-pyrone (III) reacts with phenylmagnesium bromide even at room temperature and gives the corresponding phenylcarbinol (XI) in 76% yield.

The heterocyclic γ-alcohols obtained by us can be vacuum-distilled without decomposition and are stable to storage. 2,5-Dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV) and 2,2,4-trimethyltetrahydropyran-4-ol (X) represent extremely viscous liquids. 2,2-Dimethyl-4-phenyltetrahydrothiopyran-4-ol (IX), 2,2-dimethyl-4-phenyltetrahydropyran-4-ol (XI) and 2,2,4-trimethyltetrahydrothiopyran-4-ol (VIII) are crystalline substances.

The sulfoxide (V) and the sulfones (VI, VII and XII) are completely odorless crystalline substances.

All of the described γ-alcohols, and also the sulfoxide and sulfones of the phenylthiopyranols, are insoluble in water. For this reason we were not interested in preparing the esters of these alcohols, since they cannot be subjected to pharmacological testing.

EXPERIMENTAL

2,5-Dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV). a) A solution was made up in a 3-necked flask fitted with stirrer, reflux condenser with calcium chloride tube and dropping funnel of 1.5 g of magnesium filings and 9.5 g of bromobenzene in 20 ml of absolute ether. A solution of 7 g of 2,5-dimethyltetrahydro-4-thiopyrone (I) (trans-isomer, m.p. 71°) in 25 ml of absolute ether was then added drop-wise with continual stirring and ice-water cooling to the above solution. The reaction mixture was stirred for 1 hour at room temperature and for 15 hours at the boiling point of ether. The magnesium alcoholate which formed upon ice water cooling was decomposed with dilute hydrochloric acid (1 : 1) until complete solution of the precipitate. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried over sodium sulfate. The ether was driven off and the residue was vacuum-distilled. Yield 4 g (37%) of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV) in the form of viscous liquid with the odor of the thio compound, b.p. 123-124° (2 mm).

Found %: C 70.56, 70.57; H 8.23, 8.23; S 14.22, 14.09. $C_{13}H_{18}OS$. Calculated %: C 70.30; H 8.11; S 14.40.

4.2 g of initial thiopyrone (I), b.p. 58-62° (3 mm) was returned, crystallizing in the receiver. After recrystallization from alcohol, it had m.p. 67-69°.

b) A solution of 7 g of 2,5-dimethyltetrahydro-4-thiopyrone (I) in 25 ml of absolute ether was added drop-wise with constant stirring and ice-water cooling to a solution of phenylmagnesium bromide, which was prepared from 1.5 g of magnesium and 9.5 g of bromobenzene in 25 ml of absolute ether. The reaction mass was stirred for 1 hour at room temperature and 20 hours while the ether boiled and then it was decomposed with 15% hydrochloric acid upon cooling and treated in the same manner as above. Vacuum-distillation yielded 4.4 g (41%) 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV), b.p. 123-124° (2 mm). 3.1 g of initial thiopyrone (I), b.p. 55-56° (2.5 mm) was returned unreacted. 1 g of resinous residue remained after distillation.

c) 15 ml of absolute ether and 1 g of fine lithium filings were placed in a 3-necked flask fitted with mercury-sealed stirrer, dropping funnel, nitrogen lead tube and reflux condenser with calcium chloride tube. A solution of 12 g of bromobenzene in 15 ml of absolute ether was added drop-wise with stirring to the above mixture and then 45 ml more of absolute ether was added. The reaction was carried out in a dry nitrogen atmosphere until complete solution of the lithium (boiling in the course of 1.5 hours). 7 g of 2,5-dimethyltetrahydro-4-thiopyrone (I), dissolved in 25 ml of absolute ether was added drop-wise in the course course of 2 hours with cooling (−10°) of the flask with an ice-salt mixture to the above prepared phenyllithium. The next day the reaction mixture was heated for 3 hours while the ether boiled evenly. Upon cooling with ice water, the reaction product was hydrolyzed with 50 ml of water. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried with sodium sulfate and vacuum-distilled. Yield 7 g (65%) of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV), b.p. 122-123° (1.7 mm) and 1 g of initial thiopyrone (I), b.p. 55-57° (2 mm).

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Sulfoxide of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (V). 6.5 ml of 10% sulfuric acid was added with stirring and water cooling to a solution of 2 g of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV) (b.p. 123-124° [2 mm]) in 40 ml of acetone and to this was added 2 g of crystalline potassium permanganate in small portions. Oxidation was complete in 2 hours. Manganese dioxide which formed was filtered off and washed on a filter with hot water. The combined filtrate and wash waters were extracted with ether. The ethereal extracts were dried with potash. After the ether was driven off, the residue crystallized. Upon boiling with benzene, the greater portion of the crystals dissolved but the residue could not be completely dissolved by prolonged boiling in a new portion of benzene. The undissolved residue was twice recrystallized from alcohol to yield 0.5 g of the sulfoxide of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (V) in the form of fine crystals, m.p. 231-232°, readily soluble in methanol, acetone, chloroform and moderately soluble in alcohol, ether, dioxane, very sparingly soluble in benzene; it was insoluble in water, gasoline and carbon tetrachloride.

Found %: C 65.39, 65.54; H 7.66, 7.67; S 13.46, 13.49. $C_{13}H_{18}O_2S$. Calcd. %: C 65.54; H 7.62; S 13.46.

Upon evaporating down the benzene solution, 1 g of friable precipitate came down which melted at 150-161°. Analysis showed it to be a mixture of sulfoxide and sulfone of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol.

Found %: C 63.16, 63.09; H 7.49, 7.56; S 13.10, 12.81.

Sulfones of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (VI) and (VIII). 13 ml of 10% sulfuric acid and 6 g of crystalline potassium permanganate in small portions were added gradually with water cooling and stirring to a solution of 4 g of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IV) (b.p. 123-124° at 2 mm) in 80 ml of acetone. Oxidation was complete in 2 hours. The manganese dioxide which formed was filtered off and washed on a filter with hot water. Upon standing, a voluminous precipitate (3.8 g) came down from the filtrate and almost completely dissolved in hot benzene. Upon partial evaporation of the benzene solution, a friable precipitate again came down. 5-fold fraction crystallization of the precipitate from a benzene-gasoline mixture yielded 1.1 g of the sulfone of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol, m.p. 163-164°.

Found %: C 61.90, 61.72; H 7.24, 7.27; S 12.59, 12.59. $C_{13}H_{18}O_3S$. Calcd. %: C 61.40; H 7.09; S 12.63.

We isolated also 0.6 g of the second diasterioisomeric sulfone of 2,5-dimethyl-4-phenyltetrahydrothiopyran-4-ol, m.p. 170-170.5°.

Found %: C 61.74, 61.60; H 7.19, 7.15; S 12.92, 12.80. $C_{13}H_{18}O_3S$. Calcd. %: C 61.40; H 7.09; S 12.63.

A test mixture of the above diasterioisomers melted at 159-168°.

Both of the isomeric sulfones were reasily soluble in methanol, alcohol, acetone, ether, dioxane, ethyl acetate, chloroform, benzene, difficulty soluble in carbon tetrachloride; they were insoluble in water and in gasoline.

About 2 g of an unseparated mixture of the above described stereoisomeric sulfones (VI) and (VII) remained in the mother liquors.

2,2-Dimethyl-4-phenyltetrahydrothiopyran-4-ol (IX). A solution of 11.5 g of 2,2-dimethyltetrahydro-4-thiopyrone (II)(b. p. 77-79° at 10 mm, n_D^{19} 1.4965) in 15 ml of absolute ether was added drop-wise with stirring and ice-water cooling to a solution of phenylmagnesium bromide, prepared from 2.3 g of magnesium and 15 g of bromobenzene in 35 ml of absolute ether. The reaction mixture was stirred for 1 hour at room temperature and then boiled for 2 hours. The mixture, cooled with ice water, was hydrolyzed with 15% hydrochloric acid. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried with sodium sulfate. After the ether was driven off, the residue was vacuum-distilled; yield 12 g (68%) of 2,2-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IX) in the form of very viscous liquid with the odor of the thio compound, b.p. 119-120° (2 mm).

Found %: C 70.38, 70.55; H 8.08, 8.12; S 14.12, 14.18. $C_{13}H_{18}OS$. Calcd. %: C 70.30; H 8.11; S 14.40.

Upon standing, the product partially crystallized. The crystals were separated from the liquid portion and recrystallized from methanol. Yield 2 g of crystalline phenylthiopyranol (IX) in the form of colorless fine crystals, m.p. 69-70°, readily soluble in alcohol, acetone, ester, dioxane, chloroform, carbon tetrachloride, gasoline, benzene and in hot methanol; insoluble in water. Besides phenylthiopyranol (IX), distillation yielded 3 g of initial thiopyrone (II), b.p. 52-54° (2 mm). Resinous residue 1 g.

Sulfone of 2,2-dimethyl-4-phenyltetrahydrothiopyran-4-ol (XII). a) 2 ml of 10% sulfuric acid and 1 g of crystalline potassium permanganate solution were gradually added with water cooling and stirring to a solution of 0.5 g of crystalline 2,2-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IX) (m.p. 69-70°) in 10 ml of acetone. Oxidation was complete in 2 hours. The manganese dioxide which formed was filtered off and washed with hot water on a filter. The combined filtrate and wash waters were extracted with ether and the ethereal extracts were dried with potash. After the ether was driven off, we obtained 0.5 g of crystals of the sulfone of 2,2-dimethyl-4-phenyltetrahydrothiopyran-4-ol (XII), m.p. 180-181° (from methanol).

Found %: C 61.55, 61.51; H 7.22, 7.14; S 12.99, 13.08. $C_{13}H_{18}O_3S$. Calcd. %: C 61.40; H 7.09; S 12.63.

Sulfone (XII) was readily soluble in acetone, in hot methanol, alcohol, dioxane, chloroform and benzene; it was insoluble in water, gasoline and carbon tetrachloride.

b) 10 ml of 10% sulfuric acid and 4 g of crystalline potassium permanganate were gradually added with stirring and water cooling to 3 g of the liquid portion of 2,2-dimethyl-4-phenyltetrahydrothiopyran-4-ol (IX) (b.p. 119-120° at 2 mm), dissolved in 60 ml of acetone. After 2 hours of standing, the treatment was the same as in the preceding experiment. From the ethereal extract we isolated 2.4 g of solfone (XII), which after recrystallization from methanol, melted at 180-181° and proved identical to the sulfone, which was prepared in the preceding experiment. A test mixture of the two melted at the same temperature as the individual samples.

2,2 Dimethyl-4-phenyltetrahydropyran-4-ol (XI). A solution of 6.4 g of 2,2-dimethyltetrahydro-4-pyrone (III) (b.p. 77-79° at 30 mm) in 10 ml of absolute ether was added drop-wise with stirring and ice-water cooling to a solution of phenylmagnesium bromide, prepared from 1.5 g of magnesium and 9.5 g of bromobenzene in 20 ml of absolute ether. The reaction mixture was stirred for 2 hours at room temperature. Upon cooling with ice water, the reaction product was hydrolyzed with 15% hydrochloric acid. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried with sodium sulfate. After driving off the ether, the residue almost completely crystallized. The crystals were separated from the liquid protion and recrystallized from gasoline. Yield 6.6 g 2,2-dimethyl-4-phenyltetrahydropyran-4-ol (XI), m.p. 122.5-123°. Vacuum-distillation of the liquid portion yielded 1 g of initial pyrone (III), b.p. 48-51° (2.5 mm) and 1.2 g of phenylpyranol (XI), b.p. 104-105° (2.5mm), which crystallized in the receiver and after recrystallization from gasoline had m.p. 122-123°. After distillation, the resinous residue weighed 0.5 g. The total yield of product (XI) was 7.8 g (76%).

2,2-Dimethyl-4-phenyltetrahydropyran-4-ol (XI) was in the form of colorless lustrous crystals, readily soluble in methanol, alcohol, acetone, ether, dioxane, chloroform, benzene, in hot gasoline and carbon tetrachloride; insoluble in water.

Found %: C 75.76, 75.89; H 8.89, 8.96. $C_{13}H_{18}O_2$. Calcd. %: C 75.75; H 8.74.

2,2,4-Trimethyltetrahydrothiopyran-4-ol (VIII). A solution of 4.5 g of 2,2-dimethyltetrahydro-4-thiopyrone (II) (b.p. 77-79° at 10 mm) in 7 ml of absolute ether was added drop-wise with ice-water cooling and stirring to a solution of methylmagnesium iodide, prepared from 1 g of magnesium and 6 g of methyl iodide in 10 ml of absolute ether. The reaction mixture was stirred for 2 hours while the ether boiled and then, upon ice-water cooling, it was treated with 15 % hydrochloric acid. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were shaken with sodium bisulfite solution to remove the iodide and then dried with sodium sulfate. After driving off the ether, the residue completely crystallized. Yield 3 g (60%) 2,2,4-trimethyltetrahydrothiopyran-4-ol (VIII), m.p. 82-83° (from petroleum ether).

Found %: C 60.21, 60.02; H 10.13, 10.04; S 19.90, 20.20. $C_8H_{16}OS$. Calcd. %: C 59.94; H 10.06; S 20.00.

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Thiopyranol (VIII) was in the form of colorless crystals with the odor of the thio compound, readily soluble in methanol, alcohol, acetone, dioxane, ethyl acetate, benzene, chloroform, carbon tetrachloride and in boiling petroleum ether, difficultly soluble in gasoline and completely insoluble in water.

2,2,4-Trimethyltetrahydropyran-4-ol (X). A solution of 6.4 g of 2,2-dimethyltetrahydro-4-pyrone (III) (b.p. 77-79° at 30 mm) in 10 ml of absolute ether was added drop-wise with stirring and ice-water cooling to a solution of methylmagnesium iodide, prepared from 1.5 g of magnesium and 9 g of methyl iodide in 15 ml of absolute ether. The reaction mass was stirred 1 hour at room temperature and 1 hour at the boiling point of ether and then, upon ice-water cooling, it was decomposed with 15 % hydrochloric acid. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were shaken with sodium bisulfite solution to remove iodine and dried with sodium sulfate. After the ether was driven off, the residue was vacuum-distilled. Yield 4.6 g (64%) of 2,2,4-trimethyltetrahydropyran-4-ol (X) in the form of a viscous liquid, b.p. 56-58° (1 mm), n_D^{20} 1.4569.

Found %: C 67.17, 66.95; H 11.77, 11.17. $C_8H_{16}O_2$. Calcd. %: C 66.62; H 11.18.

SUMMARY

Five tertiary heterocyclic γ-alcohols of the tetrahydropyrane and tetrahydrothiopyrane series (IV, VIII, IX, X and XI) were synthesized by the reaction of either organolithium of organomagnesium compounds with the corresponding heterocyclic γ-ketones.

As oxidation products of phenylthiopyranols (IV) and (IX) we obtained the sulfoxide (V), the two diastereoisomeric sulfones (VI) and (VII), and the sulfone (XII).

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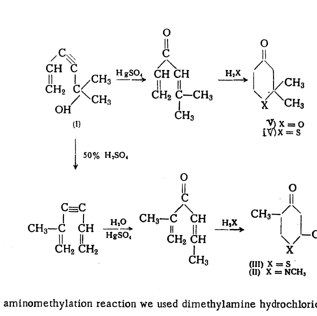
HETEROCYCLIC COMPOUNDS

36. THE MANNICH REACTION WITH HETEROCYCLIC KETONES (γ-PIPERIDONES, TETRAHYDRO-γ-PYRONES AND TETRAHYDRO-γ-THIOPYRONES)

I. N. Nazarov and E. T. Golovin

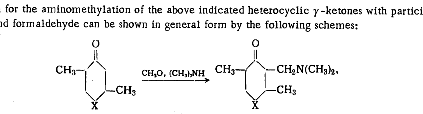
Using the aminomethylation reaction, known as the Mannich reaction [1], it is easy to obtain various β-substituted aminoketones. There is nothing in the literature on running the aminomethylation reaction with heterocyclic ketones of either the piperidine, tetrahydropyrane or tetrahydrothiopyrane series. It seemed possible to us to study the application of this reaction to the different heterocyclic γ-ketones at our disposal, the preparation of which by simple and general methods was worked out in our laboratory [2-5].

In the present paper we describe the aminomethylation of the following heterocyclic γ-ketones, obtained on the basis of the technically available dimethylvinylethynylcarbinol (I): 1,2,5-trimethyl-4-piperidone (II), 2,5-dimethyltetrahydro-4-thiopyrone (III), 2,2-dimethyltetrahydro-4-thiopyrone (IV) and 2,2-dimethyltetrahydro-4-pyrone (V):



For running the aminomethylation reaction we used dimethylamine hydrochloride and 30% aqueous formaldehyde solution.

The reaction for the aminomethylation of the above indicated heterocyclic γ-ketones with participation of dimethylamine and formaldehyde can be shown in general form by the following schemes:



X = NCH_3, S.

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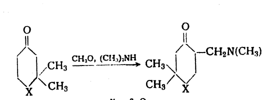
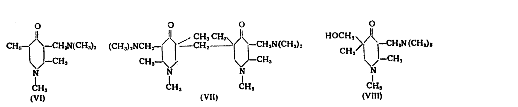


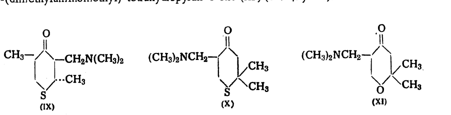
X = S, O.

The aminomethylation of 1,2,5-trimethyl-4-piperidone (II) gives 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VI) in 46.5% yield; here di-(1,2,5-trimethyl-3-dimethylaminomethyl-4-keto-5-piperidyl)-methane (VII) was isolated as by-product. The latter, under conditions favorable for its formation, was obtained in up to 31% yield. When this reaction was run with a large excess of formaldehyde (twice the theoretical amount) the main reaction product proved to be 1,2,5-trimethyl-3-(dimethylaminomethyl)-5-methylol-4-piperidone (VIII), obtained in 21% yield:



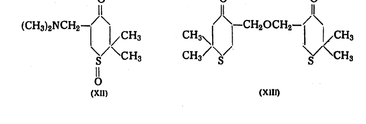
(VI) (VII) (VIII)

When dimethylamine and formaldehyde are reacted with either 2,5-dimethyltetrahydro-4-thiopyrone (III, trans-isomer), 2,2-dimethyltetrahydro-4-thiopyrone (IV) or 2,2-dimethyltetrahydro-4-pyrone (V) the corresponding dimethylaminomethyl derivatives are obtained: 2,5-dimethyl-3-(dimethylaminomethyl)-tetrahydrothiopyran-4-one (IX) (61.5% yield), 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydrothiopyran-4-one (X) (65% yield) and 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydropyran-4-one (XI) (60.5% yield):



(IX) (X) (XI)

The oxidation under mild conditions of 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydro-4-thiopyrone (X) hydrochloride, dissolved in glacial acetic acid, with 28% hydrogen peroxide gave the corresponding sulfoxide (XII), which was isolated as the hydrochloride. Attempts to obtain the sulfones of thiopyrones (IX) and (X) remained unsuccessful, since in the oxidation of their hydrochlorides with either potassium permanganate in the cold or with 28% hydrogen peroxide in acetic acid under short heating these poorly stable compounds suffer decomposition with cleavage of the β-amino group.



(XII) (XIII)

For successful aminomethylation of 1,2,5-trimethyl-4-piperidone (II) by the Mannich reaction it is necessary to cool the reaction mixture, since here the piperidone reacts very vigorously (with heat evolution) with formaldehyde and secondary amines. In the opposite case, even at room temperature, secondary reactions begin to predominate, lowering the yield of the desired product (VI), and here compound (VII) is obtained as the main product. On the other hand, with sulfur- or oxygen-containing heterocyclic γ-ketones (III, IV and V) the Mannich reaction fails to go at all at room temperature and requires heating on the water bath for its completion. It should be mentioned that the duration of heating the reaction mixture noticeably affects the yield of the aminomethylated product and in each individual case should be made as short as possible. If this is not done the yield of aminomethylated ketone is lowered due to secondary reactions, proceeding with the formation of a number of products, among which di-(2,2-dimethyl-4-ketotetrahydro-1-thio-5-pyranyl)-dimethyl ether (XIII) was isolated in the Mannich reaction with thiopyrone (IV).

The heterocyclic β-aminoketones (VI, IX, X and XI) obtained by us represent colorless liquids, capable of being vacuum-distilled without decomposition, but which cannot be stored for a long time without suffering change. The changes, taking place during their storage, lead to an elevation and "spreading" of the boiling point. Similar behavior on the part of β-aminoketones has also been repeatedly observed earlier for other examples [6, 7, etc.]. The salts of these β-aminoketones are completely stable. To characterize all of the β-aminoketones synthesized by us, we prepared their crystalline picrate and hydrochloride derivatives.

In view of the presence of asymmetric carbon atoms, β-aminoketones (VI) and IX) should represent a mixture of diastereoisomers. However, when we prepared their crystalline derivatives, only one stereoisomeric form was isolated in both cases, which, apparently, is present in predominant amount. Analagous facts have also been observed in many other cases [7, 8, etc.].

The heterocyclic β-aminoketones described by us possess undoubted interest as intermediates for the synthesis of new physiologically active substances of diverse action. In the pharmacological testing of their hydrochlorides the β-aminoketones themselves showed low activity and low toxicity. The properties studied were general action and toxicity,pain-killing and anesthetic action, and the influence on the elements of the vegetative nervous system, on smooth and cross-striated musculature.

EXPERIMENTAL

1,2,5-Trimethyl-3-(dimethylaminomethyl)-4-piperidone (VI). a) 14 g of 1,2,5-trimethyl-4-piperidone (II) (b.p. 68-70° at 9 mm, n_D^{19} 1.4604), was placed in a 3-necked flask fitted with stirrer, reflux condenser and dropping funnel and a solution of 9 g of dimethylamine hydrochloride in 10 g of 30% aqueous formaldehyde solution was added drop-wise with stirring and ice-water cooling to the flask. The homogeneous reaction mixture was stirred for 5 hours at room temperature. Upon cooling and in the presence of ether, the aqueous solution was then saturated with solid caustic soda and extracted three more times with ether. After passage of carbon dioxide gas until the solution clouded, the combined ethereal extracts were dried with sodium sulfate. The ether was driven off and 2-fold vacuum-distillation yielded 9.2 g (46.5%) 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VI) in the form of colorless liquid with an amine odor, b.p. 84-85° (4 mm), n_D^{20} 1.4758, d_4^{20} 0.9552, MR_D 58.63; calcd. 58.69.

Found %: N 14.20, 14.30. $C_{11}H_{22}ON_2$. Calcd. %: N 14.13.

Besides this, we obtained 3.2 g (16%) di-(1,2,5-trimethyl-3-dimethylaminomethyl-4-keto-5-piperidyl)-methane (VII) b.p. 170-171° (3 mm) n_D^{20} 1.5005. We also obtained 2.6 g of initial unreacted piperidone (II), b.p. 54-58° (4 mm), n_D^{20} 1.4605. The intermediate fraction, 0.7 g, b.p. 73-81° (4 mm), n_D^{20} 1.4713 partially crystallized. The crystals were separated and recrystallized from acetone, m.p. 237-238.5° (with sublimation). Found %: N 37.30, 37.22. This nitrogen-rich compound was not investigated further. After distillation, there was 2.5 g resinous residue.

Dihydrochloride of 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VI) was prepared by passage of dry hydrogen chloride until saturation into a solution of the base in absolute ether. The resulting precipitate was separated, washed on a filter with absolute ether and recrystallized from anhydrous alcohol. Fine white crystals, m.p. 151°, readily soluble in water, methanol and in hot alcohol ; insoluble in acetone.

Found %: N 9.79, 9.81; Cl 25.72, 25.95. $C_{11}H_{24}ON_2Cl_2$. Calcd. %: N 10.33; Cl 26.15.

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Picrate of aminoketone (VI) melted at 95-96° (from alcohol).

Found %: N 16.39, 16.09. $C_{17}H_{25}O_8N_5$. Calcd. %: N 16.39.

b) 14 g of 1,2,5-trimethyl-4-piperidone (II) and 9 g of dimethylamine hydrochloride were placed in a flask. 10 g of 30% aqueous formaldehyde was added drop-wise with stirring and ice-water cooling to the reaction flask. Stirring was then continued at room temperature for 5 hours. The reaction mixture was treated as in the preceding experiment. After the ether was driven off, the reaction products were twice vacuum-distilled. 1st fraction, b.p. 48-62° (3.5 mm), n_D^{19} 1.4618, 2.6 g; 2nd fraction, b.p. 83-85° (3.5 mm), n_D^{19} 1.4754, 8.9 g; 3rd fraction, b.p. 169-171° (3 mm), n_D^{19} 1.5008, 1.8 g. The 1st fraction was initial piperidone (II). The 2nd fraction was aminoketone (VI) (yield 45%). The 3rd fraction was dipiperidylmethane (VII).

c) 17 g of 1,2,5-trimethyl-4-piperidone (II) and 12.5 g of dimethylamine hydrochloride were placed in a flask. 15 g of 30% formalin was added drop-wise with stirring and (ice-salt mixture) cooling (-10°) to the reaction flask. The reaction mass was stirred for 2 hours at -10° and then for 4 hours at room temperature and treated in the usual way. Two vacuum-distillations of the reaction products yielded the following fractions: 1st, b.p. 50-65° (4 mm), n_D^{20} 1.4623, 2.5 g; 2nd, b.p. 84-86° (4 mm), n_D^{20} 1.4755, 11 g; 3rd, b.p. 175-176° (4 mm), n_D^{20} 1.5006, 2.4 g. The 1st fraction was initial piperidone (II). The 2nd fraction was aminoketone (VI) (yield 46%). The 3rd fraction was dipiperidylmethane (VII).

d) A solution of 9 g dimethylamine hydrochloride in 10 g of 30% formalin was added drop-wise with stirring to a flask containing 42 g of 1,2,5-trimethyl-4-piperidone (II); a slight evolution of heat was noticed. The reaction mass was stirred for 5 hours at room temperature and was then treated in the usual way. Three vacuum-distillations yielded 27 g of initial piperidone (II), b.p. 50-51° (4 mm), n_D^{18} 1.4602, 13 g of aminoketone (VI), b.p. 83-85° (3.5 mm), n_D^{18} 1.4746 (yield based on reacted piperidone was 65.5%) and 4 g of dipiperidylmethane (VII), b.p. 164-166° (2 mm), n_D^{18} 1.5008 (yield 19%). There was 3 g of resinous residue after distillation.

After short storage, 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VI), upon distillation, yielded higher-boiling fractions with similar refractive indices and resinous products. Thus, after 10 days of standing, fractionation of 33.5 g of product, initial b.p. 84-85° (4 mm), yielded the following fractions: 1st, b.p. 84-85° (4mm), n_D^{20} 1.4722, 6.6 g; 2nd, b.p. 86-89° (4 mm), n_D^{20} 1.4723, 4.5 g; 3rd, b.p. 90-91° (4 mm), n_D^{20} 1.4748, 8.2 g; 4th, b.p. 92-94° (4 mm), n_D^{20} 1.4763, 6.5 g; 5th, b.p. 98-101° (4 mm), n_D^{20} 1.4814, 4.3 g; 6th, b.p. 171-173° (4 mm), n_D^{20} 1.4936, 1.2 g; resinous residue 2 g.

1,2,5-Trimethyl-3-(dimethylaminomethyl)-5-methylol-4-piperidone (VIII). 9 g of dimethylamine hydrochloride and 30 g of 30% formalin were placed in a flask. 14 g of 1,2,5-trimethyl-4-piperidone (II) was added drop-wise with stirring to the flask and a slight evolution of heat was observed. Stirring was continued for 5 hours. The reaction mixture was then acidified with hydrochloric acid and treated with ether to remove the neutral products. The aqueous solution was neutralized with soda and saturated upon cooling, in the presence of ether with solid caustic soda. The free base was extracted with multiple ether extractions and after passage of a stream of carbon dioxide, was dried with sodium sulfate. Vacuum-fractionation of the reaction products yielded the following fractions: 1st, b.p. 83-86° (3.5 mm), n_D^{20} 1.4795, 1.6 g; 2nd, b.p. 94-98° (3.5 mm), n_D^{20} 1.4845, 4.7 g; 3rd, b.p. 169-171° (3.5 mm), n_D^{20} 1.5028, 3.2 g; resinous residue 4.5 g. The 2nd fraction was 1,2,5-trimethyl-3-(dimethylaminomethyl)-5-methylol-4-piperidone (VIII), a colorless liquid with an amine odor, yellowish upon standing (yield 21%): n_D^{20} 1.4845, d_4^{20} 1.0127, MR_D 64.56; calcd. 64.83.

Found %: N 12.28, 12.30. $C_{12}H_{24}O_2N_2$. Calculated %: N 12.27.

Picrate of piperidone (VIII) after recrystallization from alcohol-acetone mixture had m.p. 112-113°.

Found %: N 14.91, 15.11. $C_{18}H_{27}O_9N_5$. Calcd. %: N 15.31.

Di-(1,2,5-trimethyl-3-dimethylaminomethyl-4-keto-5-piperidyl)-methane (VII). 14 g of 1,2,5-trimethyl-4-piperidone (II), 8 g of dimethylamine hydrochloride and 10 g of 30% formalin were placed in a flask. An exothermic reaction started at once and was complete after 15 minutes. The reaction mixture was stirred at room temperature for 10 hours. The aqueous solution was treated with solid caustic soda; free base was repeatedly washed with ether, dried with sodium sulfate. After driving off the ether, the residue was vacuum-distilled; yield 4.1 g (21%) aminoketone (VI), b.p. 84-85° (4 mm), n_D^{18} 1.4750 and 6.3 g (31%)

dipiperidylmethane (VII), a very viscous yellow liquid, b.p. 170-171° (3 mm), n_D^{20} 1.5004.

Found %: N 13.48, 13.44. $C_{23}H_{44}O_2N_4$. Calcd. %: N 13.71.

Dipicrate of dipiperidylmethane (VII) melted at 127-128° (from alcohol).

Found %: N 15.84, 15.72. $C_{35}H_{50}O_{16}N_{10}$. Calcd. %: N 16.16.

2 g of initial piperidone (II), b.p. 52-56° (4 mm), n_D^{18} 1.4623, returned unreacted. Resinous residue 3.5 g.

2,2-Dimethyl-5-(dimethylaminomethyl)-tetrahydrothiopyran-4-one (X). a) 6 g dimethylamine hydrochloride, 7 g of 2,2-dimethyltetrahydro-4-thiopyrone (IV) (b.p. 77-79° at 10 mm), n_D^{19} 1.4965 and 7 g of 30% formalin were placed in a 3-necked flask fitted with stirrer and reflux condenser. To homogenize the reaction mixture, 5 ml of methanol was added and the mixture was stirred for 1 hour at 70-80°. After acidification of the mixture with hydrochloric acid, the neutral products were removed by treatment with ether. The base was separated from the aqueous solution with potash, extracted with ether, dried with sodium sulfate and after the ether was driven off, it was vacuum-distilled. Yield 6.3 g (65%) of 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydro-4-thiopyrone (X), colorless liquid with odor of thio compound, b.p. 99-101° (4 mm), n_D^{20} 1.5027.

Found %: N 6.99, 6.67. $C_{10}H_{19}OSN$. Calcd. %: N 6.96.

The ethereal extract of neutral products yielded 1.1 g of initial thiopyrone (IV).

Hydrochloride of aminothiopyrone (X) melted at 148° (from acetone). Fine white lustrous needles, readily soluble in water, methanol, alcohol, chloroform and in hot acetone, dioxane and ethyl acetate.

Found %: Cl 14.52, 14.63. $C_{10}H_{20}OSNCl$. Calcd. %: Cl 14.91.

Picrate of aminothiopyrone (X) had m.p. 114-114.5° (from alcohol), acicular light-yellow crystals.

b) 6 g of dimethylamine hydrochloride and 7 g of 2,2-dimethyltetrahydro-4-thiopyrone (IV) were placed in a flask. 7 g of 30% formalin was added with stirring. Two layers formed. 5 ml of methanol was added for homogeneity and the mixture was then stirred at room temperature for 5 hours. The reaction mixture was saturated with potash and extracted with ether. After the ethereal extracts were dried and distilled, we obtained 6.2 g of initial thiopyrone (IV), b.p. 52-54° (3 mm), n_D^{19} 1.4956.

c) 5 g of dimethylamine hydrochloride, 7 g of thiopyrone (IV) and 6 g of 30% formalin were taken for the reaction. The mixture was stirred while being heated on a boiling water bath for 1 hour. Upon treatment of the homogeneous reaction mixture with ether, a precipitate came down which was separated, washed on a filter with ether and water, and when recrystallized from benzene, had m.p. 154.5-155°. Yield 0.2 g of compound with unknown structure in the form of a fine white powder, soluble in acetone, chloroform, dioxane, in hot benzene and ethyl acetate; sparingly soluble in alcohol and carbon tetrachloride; completely insoluble in water, methanol, ether and in gasoline.

Found %: C 59.11, 59.13; H 8.14, 8.23; S 19.31, 19.31; N 3.41, 3.16.

The aqueous solution was given the usual treatment, and distillation of the reaction products under reduced pressure yielded 4.2 g (43%) aminothiopyrone (X), b.p. 95-99° (3.5 mm), n_D^{19} 1.5021.

d) 10 g of dimethylamine hydrochloride, 14.4 g of 2,2-dimethyltetrahydro-4-thiopyrone (IV) and 15 g of 30% formalin were taken for the reaction. 15 ml of methanol was added until the solution was homogeneous and the mixture was stirred with heating on boiling water bath for 5 hours. After acidification with hydrochloric acid, the reaction mass was treated with ether and the ethereal extracts of neutral products were dried with sodium sulfate. After the ether was driven off, the residue crystallized. Yield 3.5 g crystals, which contained no nitrogen, m.p. 117° (from alcohol), readily soluble in benzene and acetone, in hot methanol and alcohol, gasoline, dioxane and completely insoluble in water; proved to be di-(2,2-dimethyl-4-ketotetrahydro-1-thiopyranyl-5)-dimethyl ether (XIII).

Found %: C 58.17, 58.27; H 8.17, 8.15; S 19.24, 19.46. $C_{16}H_{26}O_3S_2$. Calcd. %: C 58.14; H 7.93; S 19.40.

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The aqueous solution was treated as usual. Distillation of the ethereal extractions of basic products yielded fractions: 1st, b.p. 98-101° (3.5 mm), n_D^{20} 1.5022, 8.5 g; 2nd, b.p. 105-112° (3.5 mm), n_D^{20} 1.5148, 2.3 g. The 1st fraction was aminothiopyrone (X) (yield 42.5%).

Sulfoxide of 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydro-4-thiopyrone (XII). 5 ml of 28% hydrogen peroxide (d_4^{20} 1.1040) was added to a solution of 1 g of the hydrochloride of 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydro-4-thiopyrone (X) (m.p. 148°) in 3 ml of glacial acetic acid and a slight evolution of heat was observed. After standing for a week, the solution was evaporated down under reduced pressure. The residue, a viscous colorless liquid, was dissolved in a small quantity of anhydrous alcohol and reprecipitated from an alcoholic solution of absolute ether. The viscous colorless oil which formed was rubbed to powder under a layer of fresh quantity of ether, separated from the ether and dried in a vacuum-desiccator over caustic potash. The resulting solid mass was very hygroscopic and quickly turned to an oil in air. After 2-fold recrystallization from a mixture of anhydrous alcohol and acetone, we obtained stable crystals of the hydrochloride of the sulfoxide of 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydro-4-thiopyrone (XII), m.p. 162°, soluble in water, methanol and in hot alcohol, insoluble in acetone.

Found %: N 5.64, 5.52. $C_{10}H_{20}SNCl$. Calcd. %: N 5.52.

2,5-Dimethyl-4-(dimethylaminomethyl)-tetrahydrothiopyran-4-one (IX). a) 6 g of dimethylamine hydrochloride, 7 g of 2,5-dimethyltetrahydro-4-thiopyrone (III) (trans-isomer, m.p. 71°) and 7 g of 30% formalin were placed in a 3-necked flask fitted with stirrer and reflux condenser. 5 ml of methanol was added and the mixture was heated with stirring on a boiling water bath for 6 hours. The homogeneous reaction mixture was acidified with hydrochloric acid and treated with ether to remove the neutral products. After drying and evaporation of ether, the residue crystallized. Yield 0.8 g of initial thiopyrone (III), m.p. 68-70° (from alcohol). In the presence of ether and with cooling, the aqueous solution was saturated with solid caustic soda and extracted three times with ether. After passage of a stream of carbon dioxide, the ethereal extracts were dried with sodium sulfate. The ether was driven off and the residue was vacuum-distilled. Yield 6 g (61.5%) 2,5-dimethyl-3-(dimethylaminomethyl)-tetrahydro-4-thiopyrone (IX), colorless liquid with odor of thio compound, b.p. 96-97° (2.5 mm), n_D^{20} 1.5034.

Found %: N 7.19, 6.93. $C_{10}H_{19}OSN$. Calcd. %: N 6.96.

After distillation, there was 1.5 g resinous residue.

Hydrochloride of aminothiopyrone (IX) had m.p. 164.5° (from acetone). It was soluble in water, methanol and in alcohol and also in hot acetone and dioxane.

Found %: Cl 14.54, 14.82. $C_{10}H_{20}OSNCl$. Calcd. %: Cl 14.91.

Picrate of aminothiopyrone (IX) melted at 137-137.5° (from alcohol). b) 7 g of 30% formalin was added to a solution of 6 g of dimethylamine hydrochloride and 7 g of 2,5-dimethyltetrahydro-4-thiopyrone (III) in 25 ml of methanol and the mixture was stirred with heating on a boiling water bath for 2 hours. Upon cooling, crystals of thiopyrone (III) formed in the reaction mixture. 5 g of 30% formalin was added and heating was continued for 3 hours more. The reaction mixture was treated as in the preceding experiment. Vacuum-distillation of ethereal extracts of basic products yielded 4.8 g (49%) aminothiopyrone (IX), b.p. 101-107° (4 mm), n_D^{18} 1.5136. The hydrochloride prepared from this fraction, melted at 164-164.5° and gave no depression with sample prepared in the preceding experiment. From the ethereal extracts of neutral products we isolated 2.5 g of initial thiopyrone (III), m.p. 69-70° (from alcohol).

2,2-Dimethyl-5-(dimethylaminomethyl)-tetrahydropyran-4-one (XI). 10 g of dimethylamine hydrochloride, 12.8 g of 2,2-dimethyltetrahydro-4-pyrone (V) (b.p. 77-79°, 30 mm, n_D^{20} 1.4500) and 15 g of 30% formalin were placed in a 3-necked flask fitted with stirrer and reflux condenser. 5 ml of methanol was added and the reaction mixture was heated while stirring on a boiling water bath for 5 hours. Upon cooling, the mixture was treated with ether to remove the neutral products. After drying and distillation of the ethereal extracts, we isolated 1 g of initial pyrone (V), b.p. 67-69° (8 mm), n_D^{20} 1.4506. The aqueous solution was saturated with alkali, the base was extracted with ether and after passage of a stream of carbon dioxide, it was dried with sodium sulfate. The ether was driven off and the residue was vacuum-distilled. Yield 11.2 g (60.5%) of 2,2-dimethyl-5-(dimethylaminomethyl)-tetrahydro-4-pyrone (XI) in the form of colorless liquid.

B.p. 83-85° (3.5 mm), n_D^{20} 1.4630, d_4^{20} 0.9768, MR_D 52.24; Calcd. 51.77.

Found %: N 7.38, 7.33. $C_{10}H_{19}O_2N$. Calcd. %: N 7.56.

After distillation, there was 4 g of resinous residue.

Hydrochloride of aminopyrone (XI) had m.p. 144° (from acetone). Fine white crystals, soluble in water, methanol, alcohol, ethyl acetate and in chloroform, also in hot acetone and dioxane.

Found %: Cl 15.53, 15.77. $C_{10}H_{20}O_2NCl$. Calcd. %: Cl 15.99.

Picrate of aminopyrone (XI) melted at 127.5-128° (from alcohol). Yellow lustrous flakes.

SUMMARY

The aminomethylation reaction by means of formaldehyde and dimethylamine was studied on nitrogen-, sulfur- and oxygen-containing heterocyclic γ-ketones (II, III, IV and V); here heterocyclic β-aminoketones (VI, IX, X and XI) were synthesized, the hydrochlorides of which were subjected to pharmacological testing.

The methylol derivative of piperidone (VIII), and also derivatives of the dipiperidylmethane (VII) and of the dithiopyranylmethyl ether (XIII), were isolated as by-products in the Mannich reaction.

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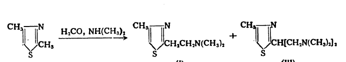
THE MANNICH REACTION IN THE THIAZOLE SERIES

B. M. Mikhailov and I. K. Platova

The condensation of organic compounds with formaldehyde and either ammonia or primary and secondary amines, known as the Mannich reaction, has found wide use as a preparative method for the introduction of aminomethyl and alkylaminomethyl groups into different types of organic substances. Into this reaction enter not only compounds with methyl and methylene groups, activated by either carbonyl or carboxyl groups, but also different heterocyclic compounds and their homologs. Thus, into the Mannich reaction enter indole [1], thiophene [2], pyrrole [3], α-picoline [4], 2-methylfuran [5], and quinaldine [4, 6], all containing sufficiently active hydrogen atoms in either the ring or the side chain.

Up to now the Mannich reaction has not been described in the thiazole series. The ability of 2-acetyl-4-phenylthiazole to react with formaldehyde and amines [7] is conditioned, naturally, not by the thiazole ring, but by the carbonyl group, and consequently this example cannot be considered as being specific for compounds of the thiazole series.

We studied the Mannich reaction in the thiazole series in application to 2,4-dimethylthiazole. It was found that the latter is quite inert toward formaldehyde and dimethylamine—the most active of the amines in the Mannich reaction. Attempts to condense 2,4-dimethylthiazole with dimethylamine in 40% aqueous formaldehyde solution under prolonged heating at various temperatures proved unsuccessful. We were able to realize the condensation by the method of boiling for a long time under reflux and ethanol solution of 2,4-dimethylthiazole with dimethylamine and paraformaldehyde in the presence of hydrochloric acid. The 2,4-dimethylthiazole partially reacts under these conditions and gives substitution products, in which both one hydrogen atom (I) and two hydrogen atoms (II) are replaced by the dimethylaminomethyl group:



(I) (III)

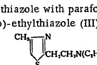
The structure of the obtained compounds can be judged on the basis of the behavior of 2,4-dimethylthiazole in its reaction with benzaldehyde. The formation here of 2-styryl-4-methylthiazole [8] shows that of the two methyl groups in 2,4-dimethylthiazole the greatest reactivity with respect to carbonyl groups is possessed by the methyl group in position 2.

4-Methyl-2-β-(dimethylamino)-ethylthiazole (I), obtained in 30% yield, is extremely unstable, and consequently it was identified as the picrate.

4-Methyl-2-di-(dimethylaminomethyl)-methylthiazole (II) is obtained in lower yield. It was identified as the methiodide.

The use of elevated temperature in running the reaction by replacing the ethyl alcohol by isoamyl alcohol failed to give an increased yield of reaction products, and only facilitated tarring.

The condensation of 2,4-dimethylthiazole with paraformaldehyde and diethylamine under the same conditions gave 4-methyl-2-β-(diethylamino)-ethylthiazole (III) in low yield:



(III)

EXPERIMENTAL

4-Methyl-2-β-(dimethylamino)-ethylthiazole (I) and 4-methyl-2-di-(dimethylaminomethyl)-methylthiazole (II). A mixture of 34 g of 2,4-dimethylthiazole [9], 24.6 g dimethylamine hydrochloride, 13.5 g paraformaldehyde, 100 ml anhydrous ethyl alcohol and 3 ml concentrated hydrochloric acid was heated on a water bath with reflux condenser for 12 hours. Upon completion of heating, the solvent was distilled off from the dark yellow solution (green opalescene). After extraction of unreacted 2,4-dimethylthiazole with ether, the residue was dissolved in 20 ml of water, the solution was saturated with potash and extracted with chloroform. The dark red chloroform extract was dried over calcined calcium chloride, the solvent was then driven off and the residue was fractionated. The following fractions were obtained: 1st, 90-92° (3 mm), 4.3 g; 2nd, 98-100° (3 mm), 1.7 g.

The 1st fraction was 4-methyl-2-β-(dimethylamino)-ethylthiazole; yield 31% based on the reacted 2,4-dimethylthiazole. The compound was very unstable and was therefore analyzed in the form of the picrate. The latter was prepared by combining hot alcoholic solutions of the components. The resulting picrate (yield 85%) after crystallization from alcohol, had m.p. 105-106.5°.

Found %: C 42.67, 42.53; H 4.25, 4.20; S 7.81, 7.75; N 17.65, 17.61. $C_{14}H_{17}O_6N_5S$. Calcd. %: C 42.29; H 4.29; S 8.02; N 17.53.

The fraction, b.p. 98-100° (3 mm), was 4-methyl-2-(dimethylaminomethyl)-methylthiazole (yield 9.4%, based on the reacted 2,4-dimethylthiazole). Due to its instability, the compound was analyzed in the form of the methiodide. Upon stirring and cooling with ice, a solution of 1.7 ml of methyl iodide was added to 1.7 g of the compound. The resulting oil rapidly crystallized upon addition of anhydrous ethyl alcohol. The precipitate was filtered off, washed with anhydrous alcohol and ether and dried. M.p. 208-209°.

Found %: C 30.41; H 5.76; N 8.32. $C_{13}H_{27}N_3SI_2$. Calcd. %: C 30.54; H 5.32; N 8.22.

Picrate had m.p. 150-151-151.5°

Found %: N 18.66. $C_{17}H_{24}O_6N_6S$. Calcd. %: N 18.64.

4-Methyl-2-β-(diethylamino)-ethylthiazole (III). A mixture of 34 g 2,4-dimethylthiazole, 33g diethylamine hydrochloride, 13.5 g paraformaldehyde, 99ml anhydrous alcohol and 3 ml concentrated hydrochloric acid was heated on a water bath for 12 hours. The alcohol was then driven off from the reaction mass and the crystallized residue was extracted with ether for extraction of initial dimethylthiazole (21 g). The resulting precipitate was dissolved in 50 ml of water, the solution was saturated with soda and extracted with chloroform. The chloroform solution was washed with aqueous soda solution, dried, and the solvent was driven off. The residue was fractionated. Yield 3 g of compound, b.p. 96-97° (2 mm).

Found %: C 60.30, 60.36; H 8.99, 9.03; S 16.14, 16.24. $C_{10}H_{18}N_2S$. Calcd. %: C 60.56; H 9.14; S 16.11.

SUMMARY

2,4-Dimethylthiazole reacts with dimethylamine and formaldehyde, forming 4-methyl-2-β-(dimethylamino)-ethylthiazole and 4-methyl-2-di-(dimethylaminomethyl)-methylthiazole.

2,4-Dimethylthiazole reacts with diethylamine and formaldehyde to form 4-methyl-2-β-(diethylamino)-ethylthiazole.

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ORGANIC INSECTOFUNGICIDES

XVIII. A NEW METHOD FOR THE PREPARATION OF ESTERS OF CHLORO- AND DICHLOROTHIOPHOSPHORIC ACIDS

Z. M. Bakanova, Ya. A. Mandelbaum, N. N. Melnikov and E. I. Sventsitsky

As is known, organic phosphorus compounds are steadily acquiring greater and greater importance in combating different plant parasites, and their scale of use in agriculture is constantly being expanded [1-4]. Diethyl chlorothiophosphate is used as starting material in the synthesis of many active contact and systemic insecticides, the preparation of which presents known difficulties. Up to now the following methods have been given in the literature for the preparation of diethyl chlorothiophosphate.

1. Reaction of sodium ethylate with phosphorus thiotrichloride [5]: $PSCl_3 + 2C_2H_5ONa = (C_2H_5O)_2PSCl + 2NaCl$. According to the data of the American investigators the yield of diethyl chlorothiophosphate in this reaction is about 50% [5]. The use of sodium ethylate is quite inconvenient due to the need of working with metallic sodium. It is also possible to obtain diethyl chlorothiophosphate by the reaction of phosphorus thiotrichloride with alcohol in the presence of sodium hydroxide [6].

2. Reaction of phosphorus thiotrichloride with anhydrous alcohol in the presence of pyridine, but the yield in this case fails to exceed 24% [7].

3. Chlorination of diethyl chlorothiophosphoric acid [8, 9] with different chlorinating agents. The yield of diethyl chlorothiophosphate by this method exceeds 70%, but the starting product here is diethyl dithiophosphoric acid, which is obtained in about 75% yield [10, 11], i. e. the final yield, based on starting crude, in this case also is only slightly more than 50%.

Ethyl dichlorothiophosphate and triethyl thiophosphate can be obtained by analogous methods [12, 13].

In view of the fact that the esters of thiophosphoric acid are of interest as raw materials for the preparation of insecticides we made a special study of different methods for the synthesis of diethyl chlorothiophosphate and other esters of thiophosphoric acid. One of the interesting new methods for the synthesis of diethyl chlorothiophosphate and triethyl thiophosphate is the reaction of aluminum ethylate with phosphorus thiotrichloride. As a result of the present study it was shown that the reaction of phosphorus thiotrichloride with aluminum ethylate proceeds in accord with the following basic schemes:

$$PSCl_3 + Al(OC_2H_5)_3 = AlCl_3 + (C_2H_5O)_3PS,$$
$$3PSCl_3 + 2Al(OC_2H_5)_3 = 3(C_2H_5O)_2PSCl + AlCl_3,$$
$$3PSCl_3 + Al(OC_2H_5)_3 = 3C_2H_5OPSCl_2 + AlCl_3.$$

Here aluminum chloroethylate is obtained together with aluminum chloride, as a result of which the yields of chlorothiophosphoric acid esters show considerable reduction. A reduction in the yield of chlorothiophosphoric acid esters is also obtained as the result of the phosphorus thiotrichloride and thiophosphoric acid esters being reduced by the aluminum alcoholate. Under the optimum conditions we were able to obtain diethyl chlorothiophosphate and ethyl dichlorothiophosphate in about 40-45% yield, which approaches the yield of diethyl chlorothiophosphate from sodium ethylate and phosphorus thiotrichloride.

EXPERIMENTAL

1. Preparation of aluminum ethylate. Fine aluminum wire, foil or powder was used to prepare aluminum ethylate. In order to accelarate the sluggish reaction of aluminum with alcohol, the aluminum was activated with mercury acetate and iodine [14]. Aluminum, absolute ethyl alcohol, about 0.1 g mercury acetate and a small iodine crystal were placed in a flask fitted with reflux condenser and closed calcium chloride tube and the reaction mixture was boiled until complete solution of the aluminum. A 2-4 fold excess of anhydrous alcohol was used to prepare the aluminum ethylate. When aluminum ethylate was prepared with an equimolecular quantity of alcohol, organic solvents, for example benzene, were used to dilute the reaction mixture. Under these conditions, the preparation of aluminum ethylate went half as fast.

2. Preparation of ethyl dichlorothiophosphate. 17 g of phosphorus thiotrichloride was placed in a flask fitted with reflux condenser and mechanical stirrer and upon cooling and stirring, a solution of aluminum ethylate, prepared from 0.5 g metallic aluminum and 3 g anhydrous alcohol in 8 ml of benzene, was added. After addition of the aluminum ethylate, the reaction mixture was heated on a water bath at 50° for 3 hours. After the reaction was complete and the reaction mixture was cooled, it was washed with ice water and acidified with hydrochloric acid. The benzene layer was separated, dried with anhydrous calcium chloride; the benzene was driven off and the ethyl dichlorothiophosphate was vacuum-distilled. Yield of pure compound was about 40%.

B.p. 68° (20 mm), d_0^0 1.3968, n_D^{25} 1.5030. According to the literature data, ethyl dichlorothiophosphate has b.p. 68° (20 mm) and d_0^0 1.3966 [15].

3. Preparation of diethyl chlorothiophosphate. A solution of aluminum ethylate, prepared from 2 g metallic aluminum and 25 ml anhydrous ethyl alcohol was gradually added with cold-water cooling to a flask fitted with reflux condenser and mechanical stirrer, containing 34 g of phosphorus thiotrichloride. After addition of all the aluminum ethylate, the reaction mixture was held at 50-60° for 2 hours. When the reaction was complete, the mixture was cooled and treated with 70 ml cold water, containing admixed hydrochloric acid. The resulting oil was separated, dried over calcum chloride and vacuum-fractionated. Yield of diethyl chlorothiophosphate was about 42%.

B.p. 96-98° (25 mm), d_0^0 1.2015, n_D^{25} 1.4670. According to the literature data, diethyl chlorothiophosphate has b.p. 96-99° (25 mm), d_0^0 1.2017 and n_D^{25} 1.4678.

SUMMARY

A new method was proposed for the preparation of chloro- and dichlorothiophosphoric acid esters by the reaction of phosphorus thiotrichloride with aluminum ethylate. The yield of chloro- and dichlorothiophosphoric acid esters by this method is greater than 40%.

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ORGANIC INSECTOFUNGICIDES

XIX. SYNTHESIS OF MIXED ESTERS OF DITHIOPHOSPHORIC ACID CONTAINING AN AMIDE GROUP IN THE ALIPHATIC ESTER RADICAL

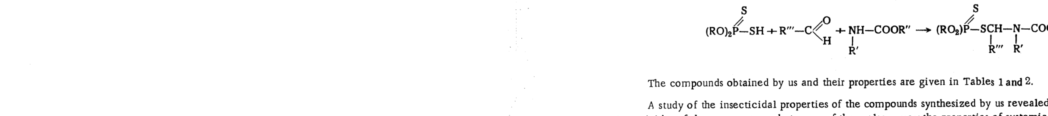
K. D. Shvetsova-Shilovskaya, N. N. Melnikov and N. I. Martemyanova

Among the organic phosphorus compounds, in recent years finding quite extensive use in agriculture, the systemic type of insecticides possess considerable interest, their distinguishing feature being the ability to move through the vascular system of plants and in the course of a variable length of time to kill the parasites, feeding on the saps of the plant treated in this manner. Up to now two types of organophosphorus compounds possessing systemic action have been described: 1) the mixed esters of thio- and dithiophosphoric acids, containing sulfide sulfur or some other functional group in the ester radical, and 2) the amides of pyrophosphoric and phosphoric acids [1-6]. One of the active compounds of the first group is "Systox"(ethylmercaptoethyldiethyl thiophosphate), and in the second—pyrophosphoric acid octamethyltetraamide. It was recently shown in our laboratory that some of the thiophosphoric acid amidoesters also show the properties of systemic insecticides, although in the duration of their effect they are somewhat inferior to the octamethyltetraamide of pyrophosphoric acid [7].

In connection with our study of the relationship between structure and the insecticidal activity of organic phosphorus compounds it seemed of interest to study the mixed esters of dithiophosphoric acid, containing amino- and amido- groups in the aliphatic radical. Only extremely few compounds of this type have been described in the literature, and it is only very recently that information has appeared on the presence of insecticidal properties in them [8]. We first undertook a study of the compounds having the general formulas (I) and (II), where R and R' are aliphatic hydrocarbon radicals:

(I) (II)

These compounds are easily obtained by the Mannich reaction in the reaction of the partial esters of dithiophosphoric acid with aldehydes and esters of carbamic acid:



The compounds obtained by us and their properties are given in Tables 1 and 2.

A study of the insecticidal properties of the compounds synthesized by us revealed that they are weak insecticides of the contact type, but some of them also possess the properties of systemic insecticides and in their activity and duration of action approach the octamethyltetraamide of pyrophosphoric acid.

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TABLE 1

Properties of Mixed Esters of Dithiophosphoric Acid of General Formula $(RO)_2P(=S)-SCH_2-N(R')-COOR''$

R	R'	R''	Yield (%)	Boiling point and pressure (in mm)	d_4^{20}	n_D^{20}	Analysis for P (%) found	Analysis for P (%) calculated
CH_3	H	C_2H_5	36.3	107–110° (0.2)	1.3498	1.5091	10.76, 10.55	11.95
C_2H_5	H	C_2H_5	42.0	64–68 (0.65)	1.1904	1.4990	10.68, 10.68	10.78
n-C_3H_7	H	C_2H_5	60.7	82 (0.075)	1.0866	1.4912	9.47, 9.41	9.82
iso-C_4H_9	H	C_2H_5	46.6	122–124 (0.175)	m.p. 22°		9.25, 9.03	9.02
C_2H_5	CH_3	C_2H_5	20.8	107–114 (0.15)	1.1814	1.5041	10.2, 10.25	10.31
C_4H_9	CH_3	C_2H_5	53.7	145–152 (0.45)	1.0675	1.4870	8.91, 8.95	8.73
iso-C_4H_9	CH_3	C_2H_5	67.7	124–127 (0.2)	1.0591	1.4840	8.22, 8.28	8.73
C_2H_5	C_2H_5	C_2H_5	52.5	108–113 (0.18)	1.0301	1.4807	10.09, 10.48	9.78
C_2H_5	C_2H_5	iso-C_3H_7	65	112–120 (0.18)	1.1182	1.4867	9.47, 9.90	9.42
iso-C_3H_7	C_2H_5	iso-C_3H_7	39.2	113–120 (0.15)	1.0560	1.4820	8.27, 8.18	8.67
C_4H_9	C_2H_5	iso-C_3H_7	70.5	136–140 (0.18)	1.0718	1.4890	–	–
C_4H_9	H	C_2H_5	80.6	100 (0.20)	1.2523	1.5000	9.07	9.02

TABLE 2

Properties of Mixed Esters of Dithiophosphoric Acid of General Formula $(RO)_2P(=S)-SCH(CH_3)-N(R')-COOR''$

R	R'	R''	Yield (%)	Boiling point and pressure (in mm)	d_4^{20}	n_D^{20}	Analysis for P (%) found	Analysis for P (%) calculated
C_2H_5	H	C_2H_5	44	74–83° (0.1)	1.1592	1.4896	10.4	10.3
iso-C_3H_7	H	C_2H_5	39.6	90–93 (0.4)	1.1008	1.4744	9.65	9.4
iso-C_4H_9	H	C_2H_5	43.3	95–114 (0.3–0.4)	1.0845	1.4906	9.35	8.68
CH_3	C_2H_5	C_2H_5	25.4	70–71 (1)	1.1826	1.4980	9.76	10.3
C_3H_7	C_2H_5	C_2H_5	18.8	75–85 (0.3)	1.0703	1.4925	8.35	8.65
iso-C_3H_7	C_2H_5	C_2H_5	33	99 (1)	1.0793	1.4780	9.1	8.65
iso-C_4H_9	C_2H_5	C_2H_5	61	92–103 (0.3)	1.0554	1.4855	8.61	8.03
CH_3	C_2H_5	iso-C_3H_7	30	65–75 (0.3)	1.0595	1.4973	10.6	10.2

EXPERIMENTAL

Preparation of the mixed esters of dithiophosphoric acid, containing the carbamido group in the aliphatic ester radical, was carried out as follows: a mixture of aldehyde with carbamic acid ester was placed in a flask fitted with reflux condenser, mechanical stirrer and dropping funnel; the partial ester of dithiophosphoric acid was gradually added with vigorous stirring to the reaction flask. Upon addition of the

partial ester of dithiophosphoric acid, the temperature of the reaction mixture gradually rose to 40-50°. On addition of the total quantity of partial ester of dithiophosphoric acid, the reaction mixture was set aside for 1-3 days at room temperature. After the reaction was complete, the resulting product was extracted with benzene, the benzene solution was washed twice with water, dried with sodium sulfate, the benzene was driven off and the residue was vacuum-fractionated. None of the prepared compounds are described in the literature.

SUMMARY

For the purpose of studying their insecticidal properties we synthesized a number of previously unknown mixed esters of dithiophosphoric acid, containing the carbamido group in the aliphatic ester radical. Most of the compounds synthesized by us appear as weak contact insecticides, but some of them also show quite strong systemic action.

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QUINOLINE AND ITS DERIVATIVES

XIII. SYNTHESIS OF QUINOLINE BASES FROM DIAMINES OF THE DIPHENYL SERIES

B. I. Adrashev and Yu. M. Kozlenko

Earlier it was shown that the syntheses of quinoline bases from diamines appear to be specific, due to the different yields and depending on the methods used for their preparation [1, 2]. In this communication we give the syntheses of a number of quinoline bases from substituted benzidines. The rules mentioned in previous papers can also be extended to these syntheses, and specifically the highest yields of quinoline bases are obtained by the Skraup reaction, the median yields by the Baeyer reaction, and the lowest yields by the Doebner-Miller reaction (see table). The best yield by Baeyer [1] and Doebner-Miller reactions is obtained with tolidine, which depends on the better solubility of the hydrochlorides formed from its biquinoline bases. Thus the mechanism of these syntheses was assumed to be in accord with [2]. The biquinoline bases, containing methyl groups in the 2,2'-positions, form substantive biquinophthalonic dyes [1, 3].

TABLE

Yields of Quinolines from Diamines of the Diphenyl Series (in %, Based on Starting Amine)

Designation of Amine	Skraup Reaction	Doebner-Miller Reaction	Baeyer Reaction
Benzidine	~60 [5]	~9 [3]	31
Tolidine	80	25	51
Dianisidine	–	~10	18
3,3'-Dichlorobenzidine	–	~10	~40

EXPERIMENTAL

Synthesis of 8,8'-dimethylbiquinoline. 7.6 g diacetyltolidine, 6.1 g p-nitrophenol, 26.2 g dehydrated glycerine, 2.2 g iron sulfate and 13.1 ml concentrated sulfuric acid (d 1.84) were placed in a half-liter round-bottomed flask. The flask was equipped with air condenser and the mixture was heated on an oil bath for 5 hours at 135-140°. Upon completion of heating, the mixture was set aside overnight and then 130 ml water was added and the mixture was heated to a boil. The hot solution was filtered free of resin. The filtrate was alkalized with 30% alkali. The precipitate was filtered off and dissolved in dilute (1 : 4) sulfuric acid. Upon cooling, the sulfate salt of the base came down and was filtered off and decomposed with soda. After purification, 8,8'-dimethylquinoline was a white, finely crystalline substance, m.p. 192°. Yield of product 5.27 g (73. 6%).

Found %: N 9.70 (Dumas). $C_{20}H_{16}N_2$. Calcd. %: N 9.85.

Synthesis of 8,8'-dimethylbiquinaldine. A mixture of 10.6 g tolidine, 12 ml hydrochloric acid and 45 ml paraldehyde was heated over a water bath for 5 hours and set aside overnight. It was then boiled with 50 ml of water and the resulting resins were filtered off. The filtrate was diluted with water to approximately 3 times its original bulk and alkalized with 30% caustic soda solution. A white resinous product formed, 21.3 g, which rapidly turned brown in the air. Upon treatment with acetone, a considerable portion of the product dissolved and after washing, there remained a white, finely crystalline precipitate of tetramethylbiquinoline, 3.41 g, which had m.p. 181°. Upon treatment with phthalic anhydride [1,4], from the filtrate we isolated 0.5 g of base, m.p. 160-165°. The total yield of tetramethylbiquinoline was 3.91 g (25.3%).

Found %: N 9.07. $C_{22}H_{20}N_2$. Calcd. %: N 8.97.

Synthesis of 8,8'-dimethoxybiquinaldine. A mixture of 12.2 g dianisidine, 22.5 ml concentrated hydrochloric acid and 45 ml paraldehyde was treated as in the preceding experiment. Yield 2.3 g (13.4%) of quinoline base, m.p. 195-200°, which after purification with acetone, caked at 248-251°. Yield of pure base

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was 1.50 g (9.0%). The picrate (from alcoholic solution) caked at 269-272°.

Found %: N 8.31. $C_{22}H_{20}O_2N_2$. Calcd. %: N 8.13.

Synthesis of 8,8'-dichlorobiquinaldine. 8.4 g of 3,3'-dichlorobenzidine, prepared from o-chloronitrobenzene was placed in a half-liter round-bottom flask and 15 ml of hydrochloric acid (d1.119) was added with stirring; the misture was cooled to room temperature and 15 ml of paraldehyde was added dropwise. The mixture was heated for 5 hours over a water bath, the flask being fitted with a reflux condenser. The mixture was set aside overnight; 50 ml of water was then added and the contents of the flask were boiled; resins were filtered from the hot solution. The filtrate was greatly diluted with water and alkalized with 30% caustic soda solution. 3.1 g of precipitate, m.p. 177-180° came down, which was the quinoline base (with resinous impurities) in mixture with unreacted dichlorobenzidine. The product was recrystallized from ether. Yield 1.15 g (9.7%) of pure base, m.p. 243°; the quinophthalones [1, 3], synthesized from the quinaldine bases, were obtained in yields of 70-75%. The biquinophthalones were dark-brown powders which did not fuse when heated at temperatures above 360°. The substantive dyes [1] prepared from them, colored cotton and silk various shades of yellow.

Analysis of biquinophthalone from 8,8'-dichlorobiquinaldine.
Found %: Cl 11.31; N 4.62. $C_{36}H_{18}O_4N_2Cl_2$. Calcd. %: Cl 11.50; N 4.57.

Synthesis of 2,2',4,4'-tetramethyldichlorobiquinoline. 8 g of 3,3'-dichlorobenzidine was stirred in 30 ml of concentrated hydrochloric acid (d 1.19) and then to this was added a mixture of 35 ml of paraldehyde and 40 ml of acetone (saturated with hydrogen chloride the previous day) and the flask was then heated for 5 hours on a water bath. The next day, the mixture was diluted with 50-70 ml of water, boiled, and the resins were filtered from the hot filtrate. After treatment of the filtrate with 30% caustic soda solution, 16 g of precipitate came down, m.p. 220°. After removal of the bases dissolved in the acetone (40 mm), pure tetramethyldichlorobiquinoline, m.p. 250°, 6.48 g (27.0%) was obtained.

From the acetone solution of bases, 2.8 g of product, m.p. 252° was obtained with the help of phthalic anhydride. The total yield of biquinoline bases was 9.28 g (37.6%). The biquinophthalone of the base was prepared, yield 74.5%.

Analysis of the biquinophthalone. Found %: Cl 11.12; N 4.41. $C_{38}H_{22}O_4N_2Cl_2$. Calcd. %: Cl 11.08; N 4.36.

The corresponding biquinophthalone dye, prepared from this intermediate, colored cotton (from a soda-alkaline bath with Glauber salt) egg-yellow, and silk (from a weakly acid bath) golden-yellow.

SUMMARY

1. From diamines of the diphenyl series we obtained 5 previously unknown biquinoline bases and 4 new substantive dyes.

2. The different yields of biquinoline bases, obtained by the Skraup, Doebner-Miller and Baeyer reactions, can be explained by the mechanism peculiarities of these reactions, showing characteristic appearance when diamines are used.

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A STUDY OF THE SULFONATION REACTION

XXXVIII. THE PREPARATION AND PROPERTIES OF 1,8-NAPHTHALENEDISULFONIC ACID

B. I. Karavaev and A. A. Spryskov

In accord with the Armstrong-Wynne rule, it is known that 1,8-naphthalenedisulfonic acid was not found in the sulfonation of 1-naphthalenesulfonic acid, whereas in the nitration of 1-naphthalenesulfonic acid the nitro group readily enters the 8 position. Consequently, to study the steric influences and nature of sulfonating forms, we attempted in the present study to show the presence of 1,8-naphthalenedisulfonic acid in the sulfonation mixture that is obtained under direct sulfonation, for which reason it was necessary to prepare and study some of the properties of this acid.

1,8-Naphthalenedisulfonic acid was first obtained in the oxidation of bis(8-sulfo-1-naphthyl) disulfide with permanganate [1]. The disulfide was obtained through the xanthate from 1-amino-8-naphthalenesulfonic acid by the Leuckart method [2]. Armstrong and Wynne [3] also made use of the same method, in addition obtaining the acid anhydride with m.p. 227° when the acid was treated with phosphorus pentachloride.

Cumming and Muir [4] treated diazotized 1-amino-8-naphthalenesulfonic acid with copper sulfate solution, reduced with sulfur dioxide. Here reaction of the reaction product with phosphorus pentachloride also gave the anhydride of the 1,8-acid with m.p. 225°. The yields of the products are not shown in the literature. The free 1,8-disulfonic acid has not been described.

EXPERIMENTAL

Preparation of 1,8-naphthalenedisulfonic acid. 24 g of twice-recrystallized (with charcoal) commercial 1,8-naphthylaminesulfonic acid was diazotized by the usual method. The filtered and washed diazonium precipitate was mixed with water and the slurry was introduced into a cooled (to 5°) solution of disulfide, prepared from 26 g of crystalline sodium sulfide and 3.5 g sulfur in 50 ml of 10% caustic soda. After 3 hours, the solution was acidified with hydrochloric acid, heated to remove hydrogen sulfide and the sulfur was filtered off. The disulfide-disulfonic acid was precipited with barium chloride as the barium salt, which upon being heated with soda solution, was converted to the sodium salt; the latter was oxidized with permanganate as described in [1]. After separation of manganese dioxide and concentration of the solution to low bulk, 16.7 g (54%) of 1,8-disulfonic acid salt crystallized out.

For conversion to the anhydride, the salt was heated with phosphorus pentachloride, phosphorus pentoxide and chlorosulfonic acid. It was found that the phosphorus compounds convert the salt to the anhydride in yields of from 35 to 55%. The best results were obtained upon heating 10 g of salt with 30 ml of chlorosulfonic acid for 2.5 hours at 55-60°. After pouring the mixture on ice, we obtained the anhydride in a yield of 85%. The recrystallized (once from dichloroethane) anhydride had m.p. 232°. Repeated recrystallizations did not raise the melting point.

After being heated for 30 minutes with 25% ammonia solution, the acid anhydride was converted to the ammonium salt of the monoamide of 1,8-disulfonic acid, readily soluble in water, separating out only upon evaporating down the solution.

Upon treatment with barium chloride in solution, the ammonium salt was converted to the barium salt of the monoamide, very sparingly soluble in cold water but readily soluble in hot water. The barium salt of the amide (dried in air) contained 4.5 moles of water of crystallization, which was removed by drying 2 hours at 110°.

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The analytical data for barium, obtained by calcination of the salt and for nitrogen, by the Dumas method, corresponded to the given formula.

Found %: Ba 19.21; N 3.64, 3.55. $C_{20}H_{16}O_{10}S_4N_2Ba$. Calcd. %: Ba 19.36; N 3.94.

When the barium salt of the amide was dissolved in water, the barium precipitated by the calculated quantity of sulfuric acid and the solution concentrated to obtain the monoamide of the 1,8-acid, the residue yielded the anhydride of the 1,8-acid. Concentration over a water bath or in vacuum at room temperature always brought about the formation of the anhydride after evaporation of water. The resulting product had m.p. 232°, gave no depression in a test mixture with the anhydride of 1,8-naphthalenedisulfonic acid and contained no nitrogen.

Thus, the monoamide of 1,8-naphthalenedisulfonic acid was converted with exceptional ease to the acid anhydride with splitting out of ammonia.

In order to prepare free 1,8-naphthalenedisulfonic acid, its anhydride was hydrolyzed upon heating on a water bath with 80% alcohol until complete solution of precipitate. After evaporation of the solution to dryness, 1,8-naphthalenedisulfonic acid was obtained in the form of colorless needles, readily soluble in water, which crystallized from 10% hydrochloric acid. Titration with alkali showed that the acid (dried in a desiccator oven caustic soda) contained 4 molecules of water of crystallization.

Found M 361.0, 361.4. $C_{10}H_8O_6S_2 \cdot 4H_2O$. Calcd. M 360.3.

Experiments were carried out to study hydrolysis of the 1,8-acid.

A weighed sample of disulfonic acid with water or with sulfuric acid was heated in a sealed tube in an Eichman apparatus. The reaction product was poured into water and naphthalene was filtered off and determined by the previously described method [5]. The sulfuric acid was determined in the filtrate gravimetrically. The increase in the amount of sulfuric acid after hydrolysis and the weight of the naphthalene which formed enabled the determination of the quantity of disulfonic acid which hydrolyzed to naphthalene and monosulfonic acid.

The experimental results, given in the table, show that 1,8-disulfonic acid hydrolyzed much more readily than the other 6 disulfo-isomers which formed upon direct sulfonation. Thus, 1,5-disulfonic acid is the most labile isomer of the latter group and after 100 hours at 100°, it hydrolyzes in the presence of 45% sulfuric acid to the extent of 5% [6], but 1,8-disulfonic acid will hydrolyze completely after only 5 hours in the presence of 38% sulfuric acid.

TABLE

Hydrolysis of 1,8 Disulfonic Acid of Naphthalene

Expt. No.	Moles of water per mole disulfonic acid	Concentration of sulfuric acid in mixture (in %)	Temperature	Duration of heating (hours)	Hydrolyzed disulfonic acid (% of taken amount)	
					to naphthalene	to monosulfonic acid
11	9.3	0	56	5	0	0
12	9.0	38.0	56	5	0	16
9	9.3	0	78	5	0	21
10	9.3	38.2	78	5	0	28
8	9.0	0	100	5	Traces	100
7	9.2	37.7	100	5	10	87
5	9.2	0	122	1	15	83

The hydrolysis of the 1,8-disulfonic acid proceeds with considerable rapidity even at 56°. The great lability of the 1,8-isomer is probably the reason it was not detected in the sulfonation mixtures prepared by direct sulfonation.

The insolubility of the 1,8-acid anhydride in water may be utilized to detect the presence of the 1,8-acid in the sulofnation mixture prepared by sulfonation of naphthalene or of 1-naphthalenesulfonic acid; the anhydride readily forms in the sulfo-mixture in the presence of sulfuric acid monohydrate or of fuming sulfuric acid.

Thus, 3 g of 1,5-naphthalenedisulfonic acid and 0.15 g of 1,8-disulfonic acid were dissolved in 20 ml of 100% sulfuric acid at room temperature and the mixture was kept at room temperature for 40 minutes. The mixture was poured in cold water and the resulting precipitate, after 24 hours, was filtered off and dried. Yield 0.08 g of 1,8-acid anhydride, m.p. 229-231°.

Thus, if the sulfonation mixture contains 5% 1,8-acid out of the total sulfonic acids present, it can be detected with this method.

1-Naphthalenesulfonic acid was sulfonated at room temp. with 92% sulfuric acid in the course of 3 to 90 days and also with 100% sulfuric acid in the presence of 5% mercuric oxide by weight of the sulfonic acid or in the presence of mercury sulfate. In the latter case the temperature was held at 0°. To form the anhydride, after sulfonation, the mixture was treated with an excess of 100% sulfuric acid and poured in water; at this point a fine precipitate always formed which caused turbidity and which dissolved after some time had elapsed. This precipitate was evidently the anhydride of 1,5 -naphthalenedisulfonic acid, the formation of which is possible under similar conditions as demonstrated by Blangey and Fierz-David [7]. Insoluble precipitated anhydride of the 1,8-acid was not found in even one case of sulfonation. It was not found even after sulfonation of 1-naphthalenesulfochloride with chlorosulfonic acid at -8°.

DISCUSSION OF RESULTS

The inability for entrance of the sulfonic group in the peri position to the sulfonic group already present in the naphthalene ring should be explained as being due to steric hindrances, which at the same time are not present in the nitration reaction. As is known, the nitrating form is the nitronium cation NO_2^+, which imitates the CO_2 molecule, and similar to the latter, is represented as the linear symmetrical particle $O = \overset{+}{N} = O$, which is shown by a study of its Raman spectra [8]. As a result, the nitronium cation can be regarded as being a rod, the entrance of which in the peri-position to the sulfonic group already present in the naphthalene nucleus is not difficult. The cation SO_3H^+ and $H_3SO_4^+$ can serve as the sulfonating agent, the theories as to the existence of which were evaluated earlier [9]. The first cation imitates the nitric acid molecule and, simialr to it, should possess a planar structure.

The second cation can only be three-dimensional with a tetrahedral structure. The probability of surmounting steric hindrances is considerably greater for the SO_3H^+ cation than for the $H_3SO_4^+$ cation due to the considerable size of the latter.

The experiments made on studying the sulfonating activity of oleum showed [10] that the $H_3SO_4^+$ cation is the most probable sulfonating form.

The practically complete absence of 1,8-naphthalenedisulfonic acid in the sulfonation products of the 1-acid also shows that the $H_3SO_4^+$ cation is the sulfonating form, rather than the SO_3H^+ cation.

SUMMARY

1. The free 1,8-naphthalenedisulfonic acid was obtained for the first time, and some of its properties were studied. A study of the hydrolysis of the 1,8-acid showed that it is the least stable isomer of the seven disulfonic acids of naphthalene.

2. A more accurate melting point for the anhydride of the 1,8-acid was found, and from it we obtained the barium salt of 1,8-naphthalenedisulfonic acid monoamide. It was shown that the monoamide of the 1,8-acid is converted into the acid anhydride when its isolation from solution is attempted.

3. The sulfonation of 1-naphthalenesulfonic acid under diverse conditions revealed the practically complete absence of 1,8-naphthalenedisulfonic acid in the sulfonation mixture; consequently, the sulfonation process most probably proceeds with the aid of the $H_3SO_4^+$ cation.

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THE REACTION OF TRICHLOROPHOSPHAZOSULFONARYLS WITH ALCOHOLS

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A study of the reaction of trichlorophosphazcsulfonaryls with alcohols was undertaken for the purpose of obtaining the previously unknown alkoxydichlorophosphazosulfonaryls and monoalkyl esters of arylsulfonamidophosphoric acids, in accord with the scheme:

$$ArSO_2N = PCl_3 + ROH \rightarrow HCl + ArSO_2N = PCl_2(OR) \qquad (I)$$

$$ArSO_2N = PCl_2(OR) + 2H_2O \rightarrow 2HCl + ArSO_2NHPO(OH)(OR). \qquad (II)$$

The trichlorophosphazosulfonaryls readily react with alcohols. The first chlorine atom reacts considerably faster than the subsequent ones; in this connection an unstable molecular compound, without the liberation of hydrogen chloride, is formed first; then, in the course of 60-90 minutes, at a temperature of 5-8° there is liberated about 0.8 equivalent of hydrogen chloride, at a rate that corresponds to a 1st order reaction. Depending on the nature of the trichlorophosphazosulfonaryl, the reaction conditions and the nature of the reaction products (their solubility), different types of substances are formed. Thus, for example, from α-trichlorophosphazosulfonnaphthyl in ether solution the crystalline, difficultly ether-soluble methoxydichlorophosphazosulfon-α-naphthyl (the dichloride of the monomethyl ester of α-naphthylsulfonimidophosphoric acid) is easily obtained in good yield by Scheme (I). If the reaction is run in such manner that the hydrogen chloride formed here is prevented from escaping, then the dichloride of α-naphthylsulfonamidophosphoric acid and methyl chloride are formed in good yield, in accord with the scheme:

$$ArSO_2N = PCl_3 + CH_3OH \rightarrow CH_3Cl + ArSO_2NHPOCl_2. \qquad (III)$$

Trichlorophosphazosulfonphenyl and -o-tolyl also react in the same manner, i. e. in the presence of hydrogen chloride they react by Scheme (III), and when the hydrogen chloride is removed they react by Scheme (I). However, in contrast to the α-naphthyl derivative, the methoxydichlorophosphazosulfonphenyl and -o-tolyl are liquids, readily soluble in ether and benzene, and failing to distill without decomposition; for this reason they cannot be obtained pure.

Trichlorophosphazosulfon-p-tolyl and -β-naphthyl also react very easily with methyl alcohol; here crystalline substances are obtained in good yields, still of unestablished structure, and not being either methoxydichlorophosphazosulfonyl compounds of the dichlorides of the free p-tolyl- and β-naphthylsulfonamidophosphoric acids.

A change in the reaction course in the presence of hydrogen chloride is fully understandable, has been observed many times, and is explained by the scheme:

$$ArSO_2N = PCl_2(OCH_3) + HCl \rightarrow CH_3Cl + ArSO_2N = PCl_2(OH). \qquad (IV)$$

The rate of Reaction (IV) depends on the nature of the aryl radical. For the phenyl derivatives Reaction (IV) proceeds rapidly (days), while for the o-tolyl and α-naphthyl derivatives it proceeds at a considerably slower rate (weeks). It is very possible that the faster rate of Reaction (IV) determines the special direction of the reaction for the p-tolyl and β-naphthyl derivatives. Probably, these derivatives momentarily give dichlorides, which condense with the still unchanged trichlorophosphazosulfonaryl molecules to yield pyrophosphoric acid derivatives, the latter then suffering partial methylation; consequently, from the trichlorophosphazosulfon-p-tolyl and -β-naphthyl it is impossible under any conditions to obtain either the methoxydichlorophosphazo compounds or the dichlorides of the free p-tolyl- and β-naphthylsulfonamidophosphoric acids.

Methoxydichlorophosphazosulfon-α-naphthyl, α-$C_{10}H_7SO_2NPCl_2(OCH_3)$ (V), when carefully hydrolyzed gives the monomethyl ester of α-naphthylsulfonamidophosphoric acid,

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$$\alpha\text{-}C_{10}H_7SO_2NHPO(OH)(OCH_3) \qquad (VI)$$

In its chemical properties (VI) behaves as a dibasic acid (to phenolphthalein), displacing carbonic acid from its salts.

The sodium salt of (VI) is considerably more stable than is the ester itself. It can easily be obtained directly from (V) by treatment with sodium hydroxide solution and crystallizes well from aqueous sodium chloride solution. With methyl alcohol (V) gives dimethoxychlorophosphazosulfon-α-naphthyl (the chloride of the dimethyl ester of α-naphthylsulfonimidophosphoric acid), $\alpha\text{-}C_{10}H_7SO_2N = PCl(OCH_3)_2$ (VII).

The already known dimethyl ester of α-naphthylsulfonamidophosphoric acid [1] is obtained in the hydrolysis of (VII). Trimethoxyphosphazosulfon-α-naphthyl [2] is obtained in good yields when either (V) or (VII) is treated with sodium methylate, which proves the structure of (V) and (VII).

The methoxydichlorophosphazosulfonphenyl and -o-tolyl were obtained as colorless transparent liquids with a pure substance content of about 68 and 62%, respectively. Their composition and structure were shown by analytical data, and by their transformation into trimethoxyphosphazosulfonphenyl and -o-tolyl, respectively.

When the trichlorophosphazosulfonaryls are reacted with alcohols, the latter taken in large excess, the corresponding trialkoxyphosphazosulfonaryls are formed first, which then show comparatively rapid and complete transformation into the dialkyl esters of arylsulfonamidophosphoric acids, in accord with the scheme:

$$ArSO_2N = P(OR)_3 + HCl \rightarrow RCl + ArSO_2NHPO(OR)_2.$$

Thus, for example, the treatment of trichlorophosphazosulfonaryls with a large excess of methyl alcohol for 1 hour gave from 9.6 to 37.5% of trimethoxyphosphazosulfonaryls and from 21.5 to 50.8% of the dimethyl esters of arylsulfonamidophosphoric acids. With ethyl alcohol under the same conditions the yields of the triethoxyphosphazosulfonaryls ranged from 26.4 to 34.1%, and of the diethyl esters from 22.7 to 45.6%. If the reaction mixture is allowed to stand at room temperature for a day, then the yield of the trialkoxyphosphazosulfonaryls drops to zero, while the yield of the dialkyl esters of the arylsulfonamidophosphoric acids rises to 80%.

EXPERIMENTAL

Order of reaction of trichlorophosphazosulfonaryls with alcohols. A solution of 0.03 mole methyl alcohol in 30.0 ml of benzene was added in the course of 2 minutes with vigorous stirring and continual passage of carbon dioxide at 5-6° to a mixture of 0.03 mole β-trichlorophosphazosulfonnaphthyl and 30.0 ml of benzene. After 1-2 minutes, the chloride had completely dissolved, indicating the formation of the intermediate addition product, which is soluble in benzene. After all the chloride had dissolved, the temperature was raised to 8-10°. The hydrogen chloride which evolved was absorbed in water and titrated (Table 1).

TABLE 1

Duration of reaction (in minutes)	Quantity of hydrogen chloride evolved (in moles)	Reaction-rate constant, calculated for reaction:	
		1st order	2nd order
10	0.00270	0.00942	0.0198
20	0.00597	0.0112	0.0248
40	0.01156	0.0121	0.0314
65	0.01662	0.0124	0.0383
80	0.01900	0.0125	0.0432

TABLE 2

Duration of reaction (in minutes)	Quantity of hydrogen chloride evolved (in moles)	Reaction-rate constant, calculated for reaction:	
		1st order	2nd order
10	0.00227	0.0257	0.191
20	0.00467	0.0315	0.285
30	0.00591	0.0298	0.313
40	0.00667	0.0275	0.325
60	0.00774	0.0251	0.370
160	0.00962	0.01 mole more of methyl alcohol was added to reaction mixture	
180	0.01017	–	–
200	0.01039	–	–
220	0.01051	–	–
240	0.01054	–	–

An experiment with 0.01 mole of trichlorophosphazosulfonphenyl in 65 ml benzene (total vol.) was performed in the same manner (Table 2).

It must be emphasized that these experiments were not devised to determine the absolute value of the reaction-rate constant, but were devised only to determine the order of the reaction and compare the reaction rate of the first and second chlorine atoms.

A comparison of the reaction-rate constants, calculated for the first and second orders, clearly shows that the reaction of trichlorophosphazosulfonaryls with methyl alcohol corresponded to the first order. Since equimolar quantities or reagents were taken, the existence of a pseudofirst order is improbable and, consequently, the splitting out of hydrogen chloride is preceded by the very rapid addition reaction which occurs without scission of hydrogen chloride and then the slowly proceeding decomposition reaction of the addition compound (1st order) takes place with splitting out of hydrogen chloride.

A comparison of the quantities of hydrogen chloride which evolved after addition of the first and second moles of methyl alcohol (for identical periods of time) shows that the first chlorine atom reacted at a considerably greater rate than the second.

Analogous data were obtained for the reaction of methyl and ethyl alcohols with o- and p-trichlorophosphazosulfonphenyls and α-trichlorophosphazosulfonnaphthyl.

Reaction of α-trichlorophosphazosulfonnaphthyl with methyl alcohol. A solution of 0.25 mole of methyl alcohol in 100 ml of ether was added at such a rate that the temperature stayed in the range 2-5°, with cooling and constant passage of a stream of dry carbon dioxide and vigorous mechanical stirring to a mixture of 0.25 mole finely ground powder of trichlorophosphazosulfon-α-naphthyl and 500 ml of dry ether. After the solution of methyl alcohol was added, stirring and passage of carbon dioxide were continued for 3 hours more. The methoxydichlorophosphazosulfon-α-naphthyl came down as fine, well-formed crystals which were separated, washed with two 30 ml portions of ether and dried in vacuum. Yield 56.5 g (66.8%).

Found %: OCH_3 9.39; Cl 20.51. Equiv. after hydrolysis 3.97 (phenolphthalein). $C_{11}H_{10}O_3NCl_2SP$. Calcd. %: OCH_3 9.18; Cl 20.97. Equiv. after hydrolysis 4.00.

When the reaction was performed in benzene solution, the yield of methoxydichlorophosphasulfon-α-naphthyl fell to 30%.

Methoxydichlorophosphazosulfon-α-naphthyl was a colorless, odorless, crystalline compound, m.p. 82-83°, insoluble in water, difficultly soluble in ether, readily soluble in benzene, acetone and in hot carbon tetrachloride.

Reaction of methoxydichlorophosphazosulfon-α-naphthyl with hydrogen chloride. A solution of 0.01 mole of methyl alcohol in 10 ml of benzene was added to a solution of 0.01 mole of α-trichlorophosphazosulfonnaphthyl in 20 ml of benzene. The flask was sealed tightly in order to allow no escape of hydrogen chloride from the reaction mixture. Gradually, in the course of a week, coarse crystals α-naphthylsulfonamidophosphoric acid dichloride precipitated out. The crystals were separated, washed with benzene and dried. Yield 76.5%. The properties corresponded to those given in the literature [1].

Reaction of trichlorophosphazosulfonphenyl and -o-tolyl with methyl alcohol. A solution of 0.03 mole methyl alcohol and 30 ml benzene was added with stirring, cooling and passage of dry carbon dioxide to a solution of 0.03 mole of trichlorophosphazosulfonphenyl in 50 ml of benzene. The temperature of the reaction mixture stayed in the range 2-5°. After 1.5 hours, the reaction was complete (about 0.03 mole hydrogen chloride evolved). The benzene was driven off and the residue was kept in vacuum (1-2 mm) at room temperature for 3 hours. The residue was an almost colorless liquid with a pungent odor, which did not distill without decomposition. Yield 8.48 g.

Found %: OCH_3 7.38. $C_7H_8O_3NSPCl_2$. Calcd. %: OCH_3 10.77.

The reaction product was readily hydrolyzed with water and formed only water-soluble compounds, consequently it did not contain either trimethoxyphosphazosulfonphenyl or dimethoxychlorophosphazosulfonphenyl, which upon hydrolysis, would yield the difficultly soluble dimethyl ester of phenylsulfonamidophosphoric acid [1]. The reaction product did not contain appreciable quantities of trichlorophosphazosulfonphenyl,

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since upon addition of the second mole of methyl alcohol to the reaction mixture, the evolution of hydrogen chloride proceeded much slower than during reaction with the first mole (see above).

Methoxylation of the reaction product yielded 61.3% trimethoxyphosphazosulfonphenyl, based on total weight of initial product, and 90.1%, based on its content of the methoxydichlorophosphazo compound (68%). The trimethoxyphosphazo compound could only have formed from methoxydichlorophosphazosulfonphenyl, since the reaction product contained neither trichloro-, nor trimethoxy-, nor dimethoxychlorophosphazo compounds (see above). Thus, by the methoxyl content of the reaction product, about 68% methoxydichlorophosphazosulfonaryl was found to be present, and by the methoxylation reaction – about 61%. Since methoxylation of pure methoxydichlorophosphazosulfon-α-naphthyl (see below) resulted in a 80.5% yield, and in other cases [1, 2] – yields of 75-95%, these data may be considered sufficiently reliable, and we can conclude that in the reaction product, the methoxyl entered chiefly into the formation of methoxydichlorophosphazophenyl and the content of the latter was close to 68%.

Under the same conditions, we prepared methoxydichlorophosphazosulfon-o-tolyl from trichlorophosphazosulfon-o-tolyl. From 9.18 g we obtained 8.9 g of nearly colorless liquid with a pungent odor which did not distill without decomposition.

Found %: OCH_3 6.34. $C_8H_{10}O_3NSPCl_2$. Calcd. %: OCH_3 10.28.

Thus, the content of methoxydichlorophosphazosulfon-o-tolyl in the reaction product was about 62%, as corroborated by the methoxylation data (see below).

Reaction of trichlorophosphazosulfonphenyl with methyl alcohol in ethereal solution. A solution of 0.1 mole of methyl alcohol in 50 ml of ether was slowly added with vigorous mechanical stirring and cooling, at such a rate that the temperature of the mixture stayed in the range 0-2°, to a mixture of 0.1 mole trichlorophosphazosulfonphenyl and 150 ml dry ether. 120-130 ml of the ether was then driven off and the solution was cooled. The dichloride of phenylsulfonamidophosphoric acid which came down was separated and washed with ether. Yield 8.5 g. 10.5 g more of product was obtained upon concentration of the mother liquors. Total yield 18.55 g (81.0%), m.p. 131-132°, gave no melting point depression with the dichloride of phenylsulfonamidophosphoric acid prepared by acidolysis of trichlorophosphazosulfonphenyl [1, 3]. The same results were obtained when carbon dioxide was passed continuously through the reaction mixture. This shows that Reaction (VI) proceeds at a very fast rate for methoxydichlorophosphazosulfonphenyl.

Preparation of dichloride of o-tolylsulfonamidophosphoric acid. Reaction (IV) goes much less readily for methoxydichlorophosphazosulfon-o-tolyl than for the phenyl derivative. Best results were obtained when the reaction was performed under the same conditions as described for the preparation of the dichloride of α-naphthylsulfonamidophosphoric acid. From 0.01 mole of trichlorophosphazosulfon-o-tolyl and 0.01 mole of methyl alcohol we obtained 1.25 g (43.6%) of the dichloride of o-tolylsulfonamidophosphoric acid with properties which corresponded to those described in the literature [1, 3].

Methoxylation of methoxydichlorophosphazosulfonaryls. A solution of 0.002 mole methoxydichlorophosphazosulfon-α-naphthyl in 20 ml of benzene was added slowly with vigorous mechanical stirring and cooling, at such a rate that the temperature stayed in the range of 3-5°, to a solution of sodium methylate, prepared from 0.004 mole of sodium and 20 ml of methyl alcohol. The reaction mixture was then heated for 30 minutes at 60°, the solvents were driven off in vacuum, and from the residue, as previously described [2], we isolated trimethoxyphosphazosulfon-α-naphthyl. Yield 0.53 g (80.5%); a mixed sample with known trimethoxyphosphazosulfon-α-naphthyl gave no melting point depression.

In this manner, from methoxydichlorophosphazosulfonphenyl and-o-tolyl, the corresponding trimethoxy compounds were prepared in yields of 90.2 and 65.5%, based on the pure methoxydichlorophosphazosulfonyl compounds. The products were identified by mixed melting points with known pure compounds.

Hydrolysis of methoxydichlorophosphazosulfon-α-naphthyl. 100 ml of water was added to 0.01 mole finely powdered methoxydichlorophosphazosulfon-α-naphthyl and the mixture was set aside overnight at room temperature. The next day a small smount of unhydrolyzed acid dichloride was sucked off on a filter and the filtrate was evaporated down in vacuum (temperature of bath not above 50°). After driving off the main bulk of water (about 90 ml), small fine transparent prisms started to come down. After 90 ml water was driven off, evaporation was stopped and the residue was cooled with ice water. The monomethyl ester

of α-naphthylsulfonamidophosphoric acid was separated, washed with two 0.5 ml portions of water and dried. Yield 1.85 g (61.4%), m.p. 95-99°, decomposed at 105°. For purification, the monomethyl ester may be recrystallized from a small amount of water.

Found %: OCH_3 9.99. Equiv. 1.94. $C_{11}H_{12}O_5NSP$. Calcd. %: OCH_3 10.30. Equiv. 2.00.

The monomethyl ester of α-naphthylsulfonamidophosphoric acid was a colorless crystalline substance, sour tasting, readily soluble in water, alcohol, acetone, insoluble in benzene, ether, carbon tetrachloride and in petroleum ether. Upon titration with caustic soda solution, the monomethyl ester took two equivalents (phenolphthalein). Upon prolonged boiling with water, it hydrolyzed to form α-naphthylsulfonamide.

Preparation of sodium salt of monomethyl ester of α-naphthylsulfonamidophosphoric acid. 0.01 mole methoxydichlorophosphazosulfon-α-naphthyl was neutralized upon heating with 1 N caustic soda solution (phenolphthalein). The solution was steamed down on a water bath until crystallization set in. The sodium salt of the monomethyl ester came down in the form of fine scales, which were suction-filtered off, washed with a small amount of sodium chloride solution and dried. For purification, the salt may be recrystallized from dilute sodium chloride solution (in water it was very readily soluble). The thus prepared sodium salt of the monomethyl ester of α-naphthylsulfonamidophosphoric acid evidently contained admixed sodium chloride.

Found %: OCH_3 8.25. $C_{11}H_{10}O_5NSPNa_2$. Calcd. %: OCH_3 8.99.

Reaction of methyl alcohol with methoxydichlorophosphazosulfon-α-naphthyl. A solution of 0.01 mole methyl alcohol in 20 ml benzene was added to a solution of 0.01 mole methoxydichlorophosphazosulfon-α-naphthyl in 30 ml benzene and the mixture was set aside at room temperature, protected from atmospheric moisture. After 15 days, the crystalline dimethoxychlorophosphazosulfon-α-naphthyl which formed was separated, washed with benzene and dried in vacuum. Yield 1.1 g (34.8%). Fine transparent prisms (from benzene), m.p. 138-140°; readily soluble in acetone, alcohol insoluble in water, carbon tetrachloride, cold benzene.

Found %: OCH_3 18.14. Equiv. 2.07. $C_{12}H_{13}O_4NSPCl$. Calcd. %: OCH_3 18.60. Equiv. 2.00.

Hydrolysis of dimethoxychlorophosphazosulfon-α-naphthyl. 0.01 mole dimethoxychlorophosphazosulfon-α-naphthyl was carefully ground, mixed with 5 ml water and neutralized at 40° with 1 N caustic soda solution (phenolphthalein). Upon cooling, the reaction mass was acidified with hydrochloric acid until acid reaction with Congo and the precipitated dimethyl ester of α-naphthylsulfonamidophosphoric acid was separated off. Yield 2.58 g (82.0%), m.p. 164-165°; identified by mixture test with known pure compound [1].

Methoxylation of dimethoxychlorophosphazosulfon-α-naphthyl was performed as in methoxylation of methoxydichlorophosphazosulfonaryls (see above). Yield of trimethoxyphosphazosulfon-α-naphthyl was 82.3%; identified by test mixture.

Reaction of trichlorophosphazosulfonaryls with excess of methyl and ethyl alcohols. 0.003 mole trichlorophosphazosulfonaryl was dissolved in 10 ml alcohol. After an hour (or after 24 hours), the solution was steamed down in vacuum to dryness and the reaction products were separated by the previously described method [2].

Yields of products from reaction of trichlorophosphazosulfonaryls with methyl and ethyl alcohols, duration of reaction 1 hour at 20°, are given in Table 3.

TABLE 3

Initial $ArSO_2N = PCl_3$	Yield (in %)			
Ar	$ArSO_2N = P(OCH_3)_3$	$ArSO_2NHPO(OCH_3)_2$	$ArSO_2N = P(OC_2H_5)_3$	$ArSO_2NHPO(OC_2H_5)_2$
C_6H_5	9.6	21.5	26.4	22.7
α-$C_{10}H_7$	37.5	34.9	27.9	38.8
β-$C_{10}H_7$	37.5	50.8	34.1	45.6

When the reaction mixture was set aside at 20° for 24 hours, only dialkyl esters of arylsulfonamidophosphoric acids are formed with yield of about 80%.

SUMMARY

1. In contrast to the reaction with alcoholates, the reaction of trichlorophosphazosulfonaryls with alcohols proceeds by different directions and very strongly depends on the nature of the aryl and the reaction conditions.

2. As a rule, the rapid removal of hydrogen chloride from the reaction sphere facilitates obtaining methoxydichlorophosphazosulfonaryls.

3. In the presence of hydrogen chloride the methoxydichlorophosphazosulfonaryls are converted into the dichlorides of arylsulfonamidophosphoric acids.

4. With alcohols some trichlorophosphazosulfonaryls fail to give either methoxydichlorophosphazo compounds or to dichlorides of arylsulfonamidophosphoric acids.

5. The hydrolysis and methoxylation of methoxydichlorophosphazosulfon-α-naphthyl was studied. The monomethyl ester of α-naphthylsulfonamidophosphoric acid was obtained.

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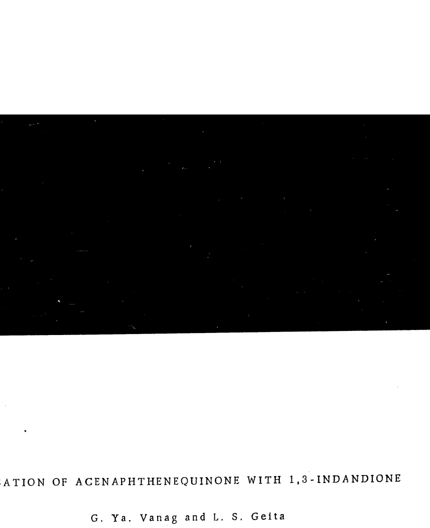
* T.p. = C. B. Translation pagination.

THE CONDENSATION OF ACENAPHTHENEQUINONE WITH 1,3-INDANDIONE

G. Ya. Vanag and L. S. Geita

In the previous paper we had shown [1] that the condensation of phenanthrenequinone with 1,3-indandione (I) fails to give the desired indigoid (III), as happens, for example, with the indandione analog hydroxythionaphthene (II), and instead the colorless 9,9-diindandionyl-10-phenanthrone (IV) is formed. It is known that acenaphthenequinone also readily condenses with hydroxythionaphthene, forming acenaphthenethionaphtheneindigo (V) [2]. For this reason it seemed of interest to also study the condensation of acenaphthenequinone with the indandione.



Acenaphthenequinone condenses with the indandione in glacial acetic acid, forming a colorless condensation product. If 1 mole of the indandione is taken for 1 mole of acenaphthenequinone, then unreacted acenaphthenequinone remains in the solution; if the condensation is run with a molar ratio of 1:2, then a pure condensation product is obtained, devoid of acenaphthenequinone as impurity. It was found that the reaction proceeds in the same manner as with phenanthrenequinone, and 2,2-di-[1', 3'-indandion-(2')-yl]-1-acenaphthenone (VI), is formed.

The diindandionylacenaphthenone is also formed in the condensation of acenaphthenequinone with the indandione in either alcohol solution or in water solution in the presence of alkali. Somewhat higher yields are obtained when the condensation is run in alcohol solution, but the product is more impure. Some of the condensation results are given in the table.

The diindandionylacenaphthenone molecule contains two active hydrogen atoms, for which reason this compound is readily soluble in alkalis, suffering enolization. The enol salts are red crystalline substances. However, it is difficult to obtain them pure, since the alkaline solutions darken rapidly and become tarry. The red dipiperidine salt crystallizes readily. This salt is quite unstable and, for example, is converted into the orange monopiperidine salt when boiled in alcohol solution.

The bonding of one of the indandionyl groups in the diindandionylacenaphthenone is comparatively labile

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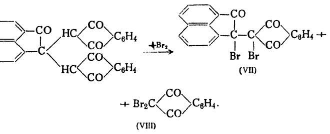
and it is cleaved with ease. Thus, for example, the action of bromine on the diindandionylacenaphthenone results in cleavage of the dibromoindandione (VIII) and 2-(bromoindandionyl)-2-bromo-1-acenaphthenone (VII) or the dibromide of the indandionyleneacenaphthenone is formed:

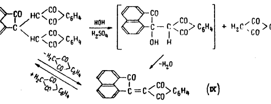


TABLE

Condensation of Acenaphthenequinone (1 Mole) with Indandione (2 Moles)

Acenaphthene-quinone (in g)	Indandione (in g)	Solvent (in ml)	Time of Condensation (in minutes)	Yields of Diindandionylacenaphthenone	
				(in g)	(in %)
		Glacial Acetic Acid			
1	1.6	30	60	1.45	58.01
1	1.6	30	90	1.69	67.61
3	4.8	100	90	5.10	68.00
1	1.6	30	120	1.92	76.81
1	1.6	30	180	2.15	86.01
3	4.8	100	180	6.40	85.33
		Alcohol			
1	1.6	50	90	2.21	88.41
1	1.6	75	90	2.25	90.01
1	1.6	50	120	2.25	90.01
1	1.6	50	180	2.27	90.80
		2N Soda + 2N Sodium Hydroxide			
1	1.6	40 + 10	120	1.4	56.01

The lability of one of the indandionyl groups in the diindandionylacenaphthenone is also characterized by its reaction with concentrated sulfuric acid. The compound dissolves in concentrated sulfuric acid with a bright-green color The condensation products of acenaphthenequinone with indoxyl and hydroxythionaphthene, i.e. the indigoïd dyes, give exactly the same green solutions in concentrated sulfuric acid. In our case it was found that the cleavage of one indandionyl group results in the formation of the indigoid compound: 2-indan-1',3'-dion-(2')-ylene-1-acenaphthenone (IX) – a red crystalline substance. The mechanism for the cleavage reaction can be depicted as follows:

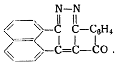


Since the indandione can add to an active double bond [3], we examined the possibility of its condensation with our obtained indandionyleneacenaphthenone. Actually, such a condensation proceeds easily, the indandione molecule adding to the ethylene double bond of the indandionyleneacenaphthenone, and again the colorless diindandionylacenaphthenone is formed.

The last reaction explains why we fail to obtain indigoid compounds in the condensation of acenaphthenequinone (and also phenanthrenequinone) with the indandione, and instead obtain diindandionyl derivatives. It can be seen that here also indigoid compounds are formed in the first phase, but the latter immediately add a second indandione molecule and give diindandionyl derivatives. The methylene hydrogen atom in indoxyl and hydroxythionaphthene is less labile than in the indandione (the influence of two carbonyl groups!), and for this reason indoxyl and the thionaphthene fail to show a tendency to add to the active double bond, and in these cases the condensation reaction stops at the formation of the indigoid compound.

In chloroform solution the indandionyleneacenaphthenone (IX) readily adds bromine at the ethylene double bond to give the colorless bromo derivative – bromoindandionylbromoacenaphthenone or indandionyleneacenaphthenone dibromide (VII). The bromine is easily cleaved when (VII) is treated with zinc dust, and again the indandionyleneacenaphthenone (IX) is formed.

The indandionyleneacenaphthenone readily condenses with hydrazine, forming the azine – a light-yellow crystalline substance (X). Indigo blue gives a similar azine [4].


(X)

EXPERIMENTAL

2,2-Di-[1',3'-indandion-(2')-yl]-1-acenaphthelene (VI). A solution of 4.8 g indandione in 20 ml glacial acetic acid and 1 ml of concentrated hydrochloric acid were added to a solution of 3 g acenaphthenequinone in 80 ml glacial acetic acid and the mixtute was brought to a boil. It was then heated on a boiling water bath for 3 hours. After one hour of heating, coarse colorless crystals began to form on the walls of the vessel. Upon completion of the reaction, the solution was cooled and the crystals were separated and washed with alcohol. Yield 6.4 g (85.3%) crude diindandionylacenaphthenone, m.p. 220-223°. After crystallization from chloroform-alcohol mixture, from glacial acetic acid or from dioxane, it had m.p. 235-236°.

Found %: C 78.45; H 3.74. $C_{30}H_{16}O_5$. Calcd. %: C 78.94; H 3.51.

Diindandionylacenaphthenone was readily soluble in chloroform-nitrobenzene, pyridine, dioxane, aniline, sparingly soluble in glacial acetic acid, acetone, carbon tetrachloride, benzene, insoluble in alcohol and ether. In concentrated sulfuric acid it dissolved with a bright-green coloration, in alkalis – orange-red.

Potassium salt. 3 g of diindandionylacenaphthenone was dissolved in 15 ml of 2 N caustic soda solution with boiling and the hot solution was sucked through a glass filter. The next day the red crystals that formed were separated, washed twice with cold water, then with alcohol and with ether. Yield 1.2 g of dipotassium salt. Readily soluble in water, sparingly soluble in alcohol. The salt was recrystallized from alcohol for analysis. Coarse red crystals.

Found %: K 13.48. $C_{30}H_{14}O_5K_2$. Calcd. %: K 14.67.

The potassium salt was covered with glacial acetic acid and boiled until the precipitate decolorized. The diindandionylacenaphthenone that formed was separated and washed with alcohol; m.p. 235-236°. The mixture with pure diindandionylacenaphthenone showed no melting point depression.

Piperidine salt. 0.5 g diindandionylacenaphthenone was dissolved with heating in 10 ml water, which contained 1 ml piperidine. Upon cooling, red rhombic crystals formed in the filtrate which were separated and washed with alcohol. Yield 0.35 g dipiperidine salt. The salt was soluble in water, alcohol and in acetone; m. p. 170-173°. The salt can be prepared equally well by solution of diindandionylacenaphthenone in 10% alcoholic solution of piperidine.

Found %: N 4.78. $C_{30}H_{16}O_5 \cdot 2C_5H_{11}N$. Calcd. %: N 4.47.

Upon boiling the dipiperidine salt with alcohol, the red solution became turbid and orange crystals of the monopiperidine salt formed; it was soluble in water and less soluble in alcohol than the dipiperidine salt. M.p. 205-206°.

Found %: N 2.85. $C_{30}H_{16}O_5 \cdot C_5H_{11}N$. Calcd. %: N 2.58.

Ethylamine salt. 0.5 g diindandionylacenaphthenone was dissolved at room temperature in 10 ml alcohol which contained 0.25 ml ethylamine. The substance slowly dissolved to form a red solution. After several days, some fine orange crystals formed in the filtrate. The precipitate increased upon addition of ether. Yield 0.1 g ethylamine salt of diindandionylacenaphthenone, m.p. 173°. The salt was soluble in water and in alcohol, sparingly soluble in acetone.

Found %: N 3.04. $C_{30}H_{16}O_5 \cdot C_2H_5NH_2$. Calcd. %: N 2.79.

Diindandionylacenaphthenone readily dissolved in dilute ammonia and also in alcoholic ammonia solution. The light-red solutions gradually darkened and browned upon standing. The ammonium salt could not be obtained in a crystalline state.

Cleavage of diindandionylacenaphthenone with concentrated sulfuric acid. 4 g of finely powdered diindandionylacenaphthenone was dissloved in 40 ml concentrated sulfuric acid with shaking for 15 minutes. The solution was sucked through a glass filter and the green filtrate was carefully poured into 300 ml of water. The red precipitate that formed was separated and washed with hot water. Yield of dry substance 3.2 g. After crystallization from chloroform, the yield was 1.95 g (71.7%) of 2-indan-1',3'-dion-(2')-ylene-1-acenaphthenone (IX), m.p. 191-192°. The substance was soluble in chloroform, pyridine, acetone, benzene and in hot glacial acetic acid; sparingly soluble in alcohol and in ether. It dissolved in concentrated sulfuric acid, producing a green coloration. With resorcin and with concentrated sulfuric acid it gave the fluorescein reaction (cleavage of phthalic acid).

Found %: C 81.83; H 3.13. M 320. $C_{21}H_{10}O_3$. Calcd. %: C 81.28; H 3.22. M 310.

After separation of the indandionyleneacenaphthenone, colorless needles, m.p. 129-130°, formed in the sulfuric acid filtrate. The substance gave all the characteristic reactions for indandione, and upon mixing with pure indandione, gave no melting point depression.

Condensation of indandionyleneacenaphthenone with indandione. 0.2 g indanionyleneacenaphthenone was heated with 10 ml alcohol. The substance partially dissolved, forming a red solution. To this 0.1 g indandione was added. After only several seconds, the red solution decolorized and the undissolved red precipitate formed colorless crystals. For completion of reaction, heating was continued for 10 minutes more and the crystals were then separated and washed with alcohol. Yield 0.29 g of diindandionylacenaphthenone. In alkalis it dissolved with red coloration and in concentrated sulfuric acid – with intense green coloration. M.p. 233-235°. The mixture with pure diindanionylacenaphthenone melted at 234-235°.

Found %: C 79.00; H 3.97. $C_{30}H_{16}O_5$. Calcd. %: C 78.94; H 3.51.

Dibromide of indandionyleneacenaphthenone (2-[2'-bromo-1',3'-indandion-(2')-yl]-2-bromo-1-acenaphthenone)(VII). 0.5 g indandionyleneacenaphthenone was dissolved in 10 ml of chloroform and a solution of 1 ml of bromine in 4 ml chloroform was added drop-wise to the red solution. The solution lightened and light crystals formed on the walls of the small flask. The contents of the flask were concentrated on a water bath and the residue was recrystallized from benzene. The crystals were separated and washed

with alcohol. Yield 0.3 g indandionyleneacenaphthenone dibromide in the form of colorless crystals, m.p. 201-203°.

Found %: Br 33.53. $C_{21}H_{10}O_3Br_2$. Calcd. %: Br 34.04.

2.5 g diindandionylacenaphthenone, 25 ml chloroform and 2 ml bromine were heated on a water bath for 1 hour. The chloroform and the excess bromine were steamed off and the remaining oil was dissolved in warm carbon tetrachloride and filtered. 0.6 g of 2,2-dibromo-1,3-indandione crystallized out of the filtrate, m.p. 177°. The mixture with pure dibromoindandione gave no melting point depression.

Found %: Br 52.20. $C_9H_4O_2Br_2$. Calcd. %: Br 52.62.

The indandionyleneacenaphthenone dibromide, which remained on the filter, was recrystallized from benzene. Yield 1.66 g, m.p. 201-203°.

Found %: Br 34.45. $C_{21}H_{10}O_3Br_2$. Calcd. %: Br 34.04.

Upon bromination of diindandionylacenaphthenone in carbon tetrachloride and in glacial acetic acid, also upon bromination with dioxane dibromide in chloroform, in all cases the same cleavage products were obtained – indandionyleneacenaphthenone dibromide and dibromoindandione.

0.5 g of indandionyleneacenaphthenone dibromide in aqueous suspension was boiled with 0.1 g of zinc dust for 30 minutes. The colorless substance gradually reddened. Crystallization of the precipitate from acetone yielded red crystals, m.p. 190-192°. The product contained no bromine and upon mixing with pure indandionyleneacenaphthenone, gave no meltingpoint depression.

Reduction with zinc dust proceeded well in alcoholic solution of acenaphthenone dibromide.

Azine of indandionyleneacenaphthenone (X). 1 g of indandionyleneacenaphthenone and 20 ml of 20% alcoholic solution of hydrazine hydrate was heated on a water bath for 30 minutes. The red substance rapidly changed to fine yellow crystals. Yield 0.8 g of the azine of indandionyleneacenaphthenone, m.p. 255-256°. It was readily soluble in glacial acetic acid, benzene, chloroform, soluble in alcohol, sparingly soluble in acetone and in carbon tetrachloride; insoluble in alkalis.

Found %: N 9.11. $C_{21}H_{10}ON_2$. Calcd. %: N 9.15.

SUMMARY

The condensation of acenaphthenequinone with indandione gives the colorless diindandionylacenaphthenone. One of its indandionyl groups is bound quite weakly and is easily cleaved, in which connection an indigoid – the red indandionyleneacenaphthenone is formed. The latter easily adds indandione and again forms the diindandionylacenaphthenone. As a result, the mechanism for the formation of the diindandionyl derivative in the condensation of indandione with acenaphthenequinone was elucidated.

The ethylene bond found in the indandionyleneacenaphthenone easily adds bromine to give a colorless dibromide. The dibromide easily cleaves bromine when treated with zinc dust to give the starting red indandionyleneacenaphthenone.

The azine of the indandionyleneacenaphthenone was obtained.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

X. THE CONDENSATION OF 1, 4-CYCLOHEXANEDIOL AND 4-CHLOROCYCLOHEXANOL WITH BENZENE

N. G. Sidorova and Yu. V. Valibekov

In the previous paper [1] it was shown that in the reaction of 1-phenylcyclohexanol with benzene there proceeds, in addition to alkylation, also reduction of the starting alcohol to phenylcyclohexane. Since phenylcyclohexanol can be regarded as being an intermediate product in the condensation of benzene with either glycols or chlorohydrins of the cyclohexane series, we studied the reaction of benzene with quinite* and with 4-chlorocyclohexanol. In the presence of aluminum chloride the aliphatic glycols react with benzene in diverse manner, depending on the character of the hydroxyl groups and the distance between them. In the presence of hydroxyls, attached to carbon atoms of different degrees of substitution, the condensation can proceed in stepwise manner [2-4]. In the case of di-tertiary glycols the reaction proceeds immediately at the expense of both hydroxyls [3]. The condensation with chlorohydrins can also proceed stepwise – the group attached to the most substituted carbon atom reacting first [5, 6].

Of the cyclic glycols only 1, 2-cyclohexanediol was used for the alkylation reaction, which with anisole in the presence of boron fluoride gave p-cyclohexylanisole, 1, 3-dianisylcyclohexane and 4, 4'-dimethoxy-m-terphenyl. Similar results were obtained with ethylene oxide in the presence of boron fluoride, and with 1, 2-dichlorocyclohexane in the presence of aluminum chloride [7]. Cyclic dihalo compounds have repeatedly been used for condensation with benzene under the influence of aluminum chloride. Here the 1, 2-dichloro- and 1, 2-dibromocyclohexanes [8] gave phenylcyclohexane and the 1, 3- and 1, 4-diphenylcyclohexanes, while 1, 2-dibromocyclopentane [9] gave phenylcyclopentane and 1, 3-diphenylcyclopentane. The reaction of 1-phenyl-1, 2-dibromocyclohexane with benzene failed to give any definite products [9].

Quinite entered into the reaction with great difficulty. With 2 equivalents of $AlCl_3$ the reaction failed to go at all, and only when the amount of $AlCl_3$ was increased to 3 equivalents did we obtain 12% of the theoretical yield of mixed 1, 3- and 1, 4-diphenylcyclohexanes. The reaction was accompanied by secondary processes, and the products were contaminated with impurities.

The reaction of 4-chlorocyclohexanol with benzene proceeded easily and gave phenylcyclohexane (with phenylcyclohexene as impurity) and a mixture of 1, 3- and 1, 4-diphenylcyclohexanes. In addition, tar was formed in all of the reactions. Its amount increased with increase in the phenylcyclohexane yield.

* 1, 4-Cyclohexanediol.

Although the qualitative composition of the reaction products was the same in all of the condensations, still the yields of the separate fractions varied greatly, depending on the reaction conditions used (amount of aluminum chloride, its moisture content, and the reaction temperature). As can be seen from the data in the table, the optimum conditions are: 1.1 equivalents of aluminum chloride, long standing of the reaction mixture at room temperature, and its short heating at 70°. With a smaller amount of aluminum chloride the reaction proceeds superficially, while with a larger amount the main product is phenylcyclohexane.

The Results of Condensing 4-Chlorocyclohexanol with Benzene in the Presence of Aluminum Chloride

Exp. Nos.	Molar ratio of reactants	Reaction conditions			Yield of reaction products (in %)		
	$ClC_6H_{10}OH$: $AlCl_3$: C_6H_6	Duration of stirring at room temperature (in days)	Length of heating (in hours)	Temperature	Phenylcyclohexane	Diphenylcyclohexanes	Total
1	1 : 1 : 22	6	1	70°	29.7	24.4	54.1
2	1 : 1 : 25	7	1	70	18.0	34.3	52 3
3	1 : 1.1 : 22	5	0.5	70	16.1	67.2	83.3
4	1 : 1.1 : 24	3	0.5	70	24.6	53.9	78.5
5	1 : 1.1 : 24	1	0.5	70	27.5	26.5	54.0
6	1 : 1.4 : 20	3	0.5	70	40.6	27.5	68.1
7	1 : 1.45 : 20	2	0.5	70	42.0	24.0	66.0
8	1 : 1.45 : 17	2	0.5	70	44.0	15.4	59.4
9	1 : 1 : 22	4	1	40—55	48.7	13.6	62.3
10	1 : 1.1 : 22	2	0.5	40—50	17.0	31.5	48.5
11	1 : 1.45 : 20	2	1	40—50	25.3	22.6	47.9
12	1 : 1 : 24	1	0.5	70	43.5	12.1	55.6 *
13	1 : 1.4 : 20	3	0.5	70	24.6	55.9	80.5 *
14	1 : 1.4 : 20	1	0.5	70	27.5	61.2	88.7 *
15	1 : 1.3 : 26	1	1	70	33.3	46.1	79.4 *

* Moist $AlCl_3$ was used.

It seemed of interest to determine the influence of moisture in the aluminum chloride in connection with the statement [10] that only moist aluminum chloride evokes the formation of propylbenzene in the condensation of allyl chloride with benzene. Moisture showed little effect on the reaction of 1-phenylcyclohexanol with benzene [1]. In the studied reaction the experiments with moist aluminum chloride gave high yields of the diphenylcyclohexanes, but for this a certain excess of it was needed when compared with anhydrous aluminum chloride. With moist aluminum chloride the reaction products showed greater purity than when ordinary aluminum chloride was used, and the second fraction consisted almost entirely of 1, 4-diphenylcyclohexane. This shows the reduced isomerizing action of aluminum chloride in the presence of water [11].

In addition, we ran the reaction between 4-chlorocyclohexanol and benzene in the presence of aluminum bromide to determine how the latter influences the formation of phenylcyclohexane. Aluminum bromide was found to be a more effective catalyst in the condensation of 1-phenylcyclohexanol with benzene [1]. In the present case it gave the same results as were obtained with aluminum chloride under similar conditions.

The isomerization, observed in the condensations of quinite and of 4-chlorocyclohexanol with benzene, proceeds in both the alkylation process and as the rearrangement result of the initially formed 1, 4-diphenylcyclohexane. The heating of the latter with benzene and aluminum chloride gives a mixture of 1, 3- and 1, 4-diphenylcyclohexanes and phenylcyclohexane. The same products were obtained from 1, 3-diphenylcyclohexane.

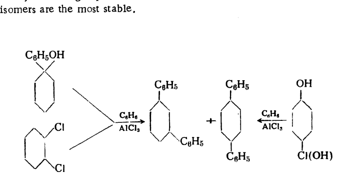
As a result, the action of aluminum chloride on 1, 3- and 1, 4-diphenylcyclohexanes produces not only their partial mutual transitions into each other, but also their cleavage with the formation of phenylcyclohexane, which supports our earlier made [1] postulation on the two paths for the formation of the latter. However, the reverse reaction is also known [12]:

$$2C_6H_5C_6H_{11} \longrightarrow C_6H_{10}\begin{matrix} \diagup C_6H_5 \\ \diagdown C_6H_5 \end{matrix} + C_6H_{12}$$

Apparently, these processes have place in the condensation of 4-chlorocyclohexanol with benzene. In this way the fact that condensation with 1 equivalent of aluminum chloride at low temperature gave phenylcyclohexane as the main product can be explained, while at the same time its yield was always lower under more drastic conditions. This suggests that phenylcyclohexane can be an intermediate product in the formation of diphenylcyclohexanes.

In the reaction of 4-chlorocyclohexanol with benzene the reaction, apparently, proceeds at first with only one functional group involved, but the 4-phenylcyclohexanol and 4-phenylcyclohexyl chloride that are formed here react further with benzene in two directions, forming phenylcyclohexane and diphenylcyclohexanes, which readily migrate into each other under the reaction conditions.

The fact that a mixture of 1, 3- and 1, 4-diphenylcyclohexanes is formed, on the one hand, as the result of isomerization with the removal of phenyl groups, as was the case in the condensation of 1-phenylcyclohexanol [1] and of 1, 2-dichlorocyclohexane [8] with benzene, and on the other hand, as the result of partial isomerization with closer proximity of these groups, as was true in our case, suggests that of all of the isomeric diphenylcyclohexanes these isomers are the most stable.



EXPERIMENTAL

1, 4-Cyclohexanediol (quinite) was prepared by hydrogenation of hydroquinone in the presence of Raney nickel (10% of weight of hydroquinone) at 130-170° and 100 atm. hydrogen pressure. The reaction was carried out in a 0.5-liter rotating autoclave in ethyl alcohol solution. Yield 80-85%. There resulted a mixture of cis- and trans-quinites which were used unseparated for further work.

4-Chlorocyclohexanol [13] was prepared by heating quinite with hydrochloric acid (molar ratio 1:1) at 80-90° for 10 hours. Yield 47%. B.p. 105-110° (10 mm).

Condensation of quinite with benzene. The reaction was performed in a 3-necked flask fitted with thermometer, mechanical stirrer and reflux condenser connected to a calcium chloride tube and an outlet tube for hydrogen chloride. 20 g (0.15 mole) of finely powdered aluminum chloride was added in small portions with mechanical stirring to a suspension of 5.8 g (0.05 mole) quinite in 90 ml (1 mole) benzene and the reaction mass was then heated for 4 hours at 70°. Decomposition was performed with ice water, acidified with hydrochloric acid. The benzene layer was washed 2-3 times with dilute hydrochloric acid, then with water, was dried with potash and fractionated. A substance was obtained with b. p. 150-200° (12 mm), 1.2 g (10%, based on diphenylcyclohexane), which was a viscous oily brick-red liquid. This fraction consisted mainly of 1, 3- and

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1, 4-diphenylcyclohexanes, since upon dehydrogenating it with selenium at 350-380°, m-terphenyl was obtained (m.p. 88°) with an admixture of p-terphenyl (m.p. 210°). Both of these substances gave no melting point depression upon being mixed with known samples of m- and p-terphenyls.

Condensation of 4-chlorocyclohexanol with benzene in the presence of aluminum chloride. For these reactions, the same apparatus and the same order of addition of the reagents was used as in the preceding case. After addition of all the aluminum chloride, the reaction mixture was stirred at room temperature and then heated on a water bath. In the reactions in which the effect of moisture was studied, after addition of aluminum chloride to the reaction mixture, several drops of water were added and the reaction was concluded in the usual manner. The separation of products was as usual. Distillation always yielded two fractions: 1st – phenylcyclohexane (with admixture of phenylcyclohexene), b.p. 95-105° (8 mm); 2nd – mixture of 1, 3- and 1, 4-diphenylcyclohexanes, b.p. 170-190° (8 mm). A resinous residue remained after distillation. Only in one case was a fraction with b. p. 140-150° (16 mm) obtained. Evidently, it contained phenylcyclohexanol. We could not repeat this result. The results of the condensation are given in the table. The first fraction gave a positive reaction for double bond and a negative one for halide. To remove phenylcyclohexene, the fraction was treated with warm sulfuric acid (d 1.76), then washed with water, dried with calcium chloride and distilled over sodium. After this purification, phenylcyclohexane had b.p. 110° (10 mm), d_4^{20} 0.9489, n_D^{20} 1.5292. For purposes of identification we prepared p-nitrocyclohexylbenzene, m.p. 57° and p-cyclohexylacetanilide, m.p. 128°. The second fraction was a light-yellow mixture of liquid 1, 3-diphenylcyclohexane and 1, 4-diphenylcyclohexane crystals. After recrystallization from alcohol, 1, 4-diphenylcyclohexane melted at 168-169°. It was dehydrogenated with selenium at 350-380° and gave p-terphenyl, m.p. 210°. Upon dehydrogenation, the liquid portion gave m-terphenyl, m.p. 88° and a small amount of p-terphenyl. Both of these compounds were identified by mixture tests with known samples.

Condensation of 4-chlorocyclohexanol with benzene in the presence of aluminum bromide. The reaction was carried out in the same manner as the condensations in the presence of aluminum chloride. Taken: 6.7 g (0.05 mole) 4-chlorocyclohexanol, 90 ml (1 mole) benzene and 19.3 g (0.072 mole) $AlBr_3$. After addition of all the aluminum bromide, the reaction mixture was stirred for 24 hours at room temperature and then heated for 30 minutes at 70°. Yield 3.5 g (43.5%) phenylcyclohexane, b.p. 107-115° (10 mm) and 3.0 g (25.5%) of a mixture of 1, 3- and 1, 4-diphenylcyclohexanes, b.p. 185-195° (10 mm). The last fraction was a mixture of liquid with crystals (m.p. 169°). From phenylcyclohexane we prepared the nitro compound, m. p. 57°; the diphenylcyclohexanes were identified by dehydrogenation with selenium at 350-380° to m- and p-terphenyl (m.p. 88 and 210°).

Reaction of 1, 4-diphenylcyclohexane with $AlCl_3$. 1.5 g of finely ground aluminum chloride was gradually added with constant stirring to a solution of 3 g of diphenylcyclohexane in 50 ml benzene. The reaction mixture was stirred at room temperature for 2 hours and then heated on a water bath at 70° for 30 minutes. The mixture was decomposed with ice water, acidified with hydrochloric acid, the benzene layer was washed with water and dried with calcium chloride and fractionated. Distillation yielded 0.7 g phenylcyclohexane, b. p. 110-115° (15 mm) and 1.4 g of a mixture of 1, 3- and 1, 4-diphenylcyclohexanes, b.p. 150-200° (14 mm). The first fraction did not contain phenylcyclohexene (negative reaction for double bond). Upon standing, some crystals of 1, 4-diphenylcyclohexane, m. p. 169° came down from the second fraction. The same results were obtained by the action of aluminum chloride on 1, 3-diphenylcyclohexane.

SUMMARY

1. The reaction of quinite with benzene in the presence of aluminum chloride yields 1, 3- and 1, 4-diphenylcyclohexanes in small amount.

2. The reaction of 4-chlorocyclohexanol with benzene in the presence of either $AlCl_3$ or $AlBr_3$ proceeds in two directions: a) alkylation proceeds with the formation of 1, 3- and 1, 4-diphenylcyclohexanes, and b) there is formation of a considerable amount of phenylcyclohexane with phenylcyclohexene as impurity.

3. Under the influence of aluminum chloride there is partial isomerization of 1, 4-diphenylcyclohexane into phenylcyclohexane and 1, 3-diphenylcyclohexane.

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A NEW SYNTHESIS OF β-4-NITROPHENYL-β-ALANINE

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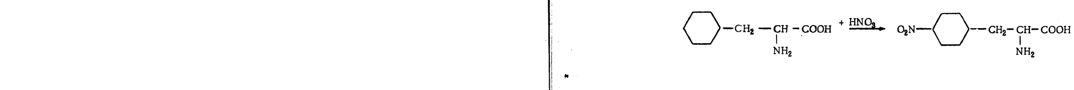
For the purpose of studying the physiological properties of β-amino acids we decided to synthesize the β-analogs of the more important α-amino acids, and first we decided to synthesize β-4-hydroxy-3, 5-diiodophenyl-β-alanine – "β-diiodotyrosine". This substance is most conveniently prepared by the direct iodination of β-4-hydroxyphenyl-β-alanine, in the future called β-tyrosine. The latter was first obtained by Posner [1] in very low yield from the rather difficultly available p-hydroxycinnamic acid. It seemed to us that β-4-nitrophenyl-β-alanine could prove to be a sufficiently good starting material for the synthesis of the corresponding hydroxyamino acid. β-4-Nitrophenyl-β-alanine was also obtained by Posner [2] by the constant boiling of p-nitrocinnamic acid with alcoholic hydroxylamine solution for 240 hours. Since this method did not permit our obtaining the needed nitroamino acid easily and in large amounts, it became necessary for us to find a preparative method for the synthesis of β-4-nitrophenyl-β-alanine.

Our preliminary experiments revealed that the application of the V. M. Rodionov reaction to p-nitrobenzaldehyde also cannot serve as a satisfactory method for the preparation of the needed amino acid (the yield failed to exceed 10%), as a result of which we turned to the direct nitration of β-phenyl-β-alanine. It is known that in the nitration of β-phenylalanine, according to the data of Erlenmeyer and Lipp [3], β-4-nitrophenylalanine is formed in almost quantitative yield. The nitration of aromatic β-amino acids has not been studied.

As a result of a number of experiments we selected the optimum conditions for the nitration of β-phenyl-β-alanine: the reaction was run at 5-8° by the method of adding a very slight excess of nitric acid (d 1.51) to a solution of the amino acid in concentrated sulfuric acid. The reaction product was isolated as the sulfate, in which connection its total yield was 76 %. The structure was established by the method of potassium permanganate oxidation, followed by the separation of the mixed isomeric nitrobenzoic acids using the Griess method [4]. Here we were able to isolate p-nitrobenzoic acid (56% of the total amount of oxidation products), m-nitrobenzoic acid (25%) and an unidentified substance with m. p. 123-125° (3.3%). Unfortunately, we were unable to conclusively establish the presence of o-nitrobenzoic acid, probably due to its greater tendency to oxidize than is shown by the other isomeric nitrobenzoic acids. As a result, it must be assumed that the nitration of β-phenyl-β-alanine, in contrast to the α-isomer, leads to a mixture of nitroamino acids, in which connection the para- and meta- isomers are formed in appreciable and comparatively similar amounts; the amount of the o-nitroamino acid is probably small:



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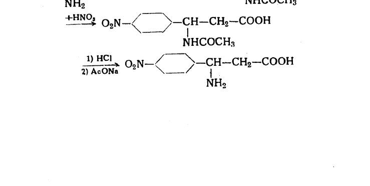
It is interesting to compare these results with some of the data, obtained in the nitration of various aromatic and fatty-aromatic (aralkyl) amines. Thus, the nitration of trimethylphenylammonium sulfate leads exclusively to the formation of the meta- isomer. In the case of trimethylbenzylammonium sulfate the meta-isomer is formed in 88 % yield, while trimethyl- (β-phenylethyl)-ammonium sulfate already gives a mixture of the ortho- and para- isomers in a total yield of 81% [5]. As a result, with its removal away from the aromatic ring the influence of the positively charged ammonium grouping is weakened, and ortho- and para-orientation appears, characteristic for alkyl substituents. Probably, in our case also there exists the concurrent influence of alkyl side chain and ammonium nitrogen, which serves to explain the appearance of the meta-isomer, not observed in the case of nitrating the corresponding α-amino acid.

Proceeding from these theoretical considerations, we decided to nitrate N-acylated β-phenyl-β-alanine, the nitrogen of which is incapable of migrating into the ammonium state, which should essentially decrease the possibility of forming the meta- isomer, and, actually, in the nitration of N-benzoyl-, N-carbomethoxy- and N-acetyl-β-phenyl-β-alanine the p-nitro derivatives were obtained in high yield. The structure of N-acetyl-β-4-nitrophenyl-β-alanine was shown by oxidation to p-nitrobenzoic acid. The behavior of these acyl derivatives under acid hydrolysis conditions is interesting: at the same time that the hydrolysis of the carbomethoxy derivative fails to proceed even under prolonged (many hours) boiling with concentrated hydrochloric acid, while the benzoyl derivative shows partial hydrolysis under these conditions, the N-acetyl-β-4-nitrophenyl-β-alanine under acid hydrolysis easily and smoothly yields the corresponding amino acid.

All of the above data permitted us to develop a convenient preparative method for obtaining β-4-nitrophenyl-β-alanine by the following scheme:



To further characterize the β-4-nitrophenyl-β-alanine we prepared the corresponding β-ureido acid and dihydrouracil, and also the ethyl ester of N-acetyl-β-4-nitrophenyl-β-alanine.

EXPERIMENTAL

Nitration of β-phenyl-β-alanine. β-Phenyl-β-alanine was prepared according to T. Johnson [6]. Yield 50.5%. M. p. 213-213.5° (with decomp.). 6.66 g (0.04 mole) of the amino acid was dissolved with stirring in 10.8 ml (20 g) sulfuric acid (d 1.84) and the reaction mixture heated to 25-30°. The homogeneous solution was cooled to 0° and 2 ml (3.06 g, 0.047 mole) of nitric acid (d 1.51) (temperature of reaction mixture 5-8°) was added to the solution drop-wise with vigorous stirring, the mixture was stirred 15-20 minutes more at room temperature and then poured on ice. Yield 3.41 g substance, m. p. 230° (with decomp.); after recrystallization from water, it had m. p. 229-230° (with decomp.). The substance gave a positive reaction for SO_4 ion while percentage analysis showed it to be the neutral sulfate of the mononitro derivative.

Found %: C 41.47, 41.50; H 4.46, 4.51; N 10.86, 10.68. $(C_9H_{10}O_4N_2)\cdot H_2SO_4$. Calculated %: C 41.72; H 3.92; N 10.80.

The wash waters were combined with the acidic mother liquor and the combined liquor was heated almost to a boil and neutralized with a hot suspension of lead carbonate (Congo). The precipitate was repeatedly washed with hot water by decanting until the yellow coloration of the solution disappeared, separated and twice washed with hot water on a filter. The filtrate, combined with the wash waters, was saturated with hydrogen sulfide, the precipitate was decanted, filtered off and the resulting solution was at first steamed down over a wire gauze, then on a water bath. Gradual concentration yielded 4 portions of substance: 0.83 g (m. p. 213°, with decomp.), 1.66 g (m. p. 213°, with decomp.), 0.93 g (m. p. 207.5° with decomp.), 0.2 g (m. p. 206.5°, with decomp.). After addition of a small quantity of alcohol to the mother liquor, 0.05 g more of substance, m. p. 200° (with decomp.), came down. Total yield 3.67 g. Analysis of sample of substance with m. p. 213°:

Found %: C 51.29, 51.21; H 4.87, 4.95; N 13.49, 13.31. $C_9H_{10}O_4N_2$. Calculated %: C 51.45; H 4.80; N 13.35.

Total yield of nitroamino acid 6.43 g (76%), 2.76 g of it recalculated on 3.41 g of its sulfate.

Oxidation of nitration products. 15.9 g (0.08 mole) mixture of nitroamino acid and its sulfate, prepared by nitration of 15 g β-phenyl-β-alanine was added to a solution of 55 g (0.35 mole) potassium permanganate in 660 ml water, the calculated quantity of potash was added to neutralize the sulfuric acid and the reaction mixture was boiled for 4 hours. The precipitate of manganese dioxide was repeatedly washed with hot water by decantation, the wash waters were combined with the main bulk of solution and steamed almost to dryness. The solid precipitate was dissolved in hot water and poured into a hot solution of hydrochloric acid (1:3). 8 g mixture of nitrobenzoic acids (A) (64%) was obtained. The filtrate was repeatedly extracted with ether; from the ethereal extractions was isolated 0.31 g dark-brown oily substance which was not investigated further.

Mixture A was dissolved in approximately 800 ml hot water, filtered, and the precipitate which came down upon cooling was separated off. Yield 4 g substance, m. p. 200° (B). The substance, recrystallized from benzene, had m. p. 233-235° and gave no melting point depression in test mixture with p-nitrobenzoic acid. The mother liquor of A was steamed down, neutralized with hot barium hydroxide solution and precipitate (C) was separated, the mother liquor was then acidified with hydrochloric acid (1:3) on Congo. 0.78 g of substance came down and 0.55 g more of substance (D) came down from the filtrate, m. p. 133-134°. After recrystallization from water and benzene, it had m. p. 139-140° and gave no melting point depression in mixture with sample of m-nitrobenzoic acid. Residue (C) was repeatedly extracted with small portions of water, the aqueous extracts were combined and neutralized with hydrochloric acid; 0.25 g substance,

m. p. 120° was separated from the filtrate; after two recrystallizations from water, it had m. p. 125°. A mixed melting point test with o-nitrobenzoic acid gave a considerable depression. Due to the minute quantities of this substance, further investigation was not carried out. Residue (C) was dissolved in approximately a 30-fold quantity of hot water and acidified (Congo). Yield 0.45 g substance with m. p. 128-130°, 0.2 g more of same substance from filtrate; it was m-nitrobenzoic acid. Resolution of the mixture of isomeric nitrobenzoic acids yielded p-nitrobenzoic (4.45 g, 56%) and m-nitrobenzoic (2 g, 25%) acids and a substance with m. p. 125° (0.25 g, 3.3%). Presence of o-nitrobenzoic acid not detected.

Nitration of N-benzoyl-β-phenyl-β-alanine. N-benzoyl-β-alanine was prepared by benzoylation of the corresponding amino acid (Schotten-Baumann), yield 92.6 %, m. p. 194-195.5°. Literature data: m. p. 194-195° [7].

a) 5 g (0.018 mole) powdered benzoyl derivative was mixed, upon vigorous stirring and cooling to 0°, with 8.3 ml sulfuric acid (d 1.84) and to this suspension, drop-wise, was added 0.8 ml (1.21 g, 0.019 mole) nitric acid (d 1.51) at 0-5°, the reaction mass was stirred for 1 hour at room temperature and then poured on ice. A resinous precipitate came down which could not be crystallized.

b) 9.54 g (0.035 mole) finely ground N-benzoyl-β-phenyl-β-alanine was gradually added to a nitrating mixture (cooled to −16°), prepared from 3 g (0.037 mole) ammonium nitrite and 30 ml (16.3 g) sulfuric acid (d 1.84) at such a rate that the temperature did not rise above 6°. The viscous mixture was stirred for 1 hour more and poured on ice. Yield about 12 g of resinous substance which softened at 30°. It was soluble in methyl and ethyl alcohol, ethyl acetate and in glacial acetic acid but was insoluble, even upon heating, in concentrated hydrochloric acid. After many months of standing, the substance crystallized. A sample, twice recrystallized from dilute acetic acid, melted at 173-175° with decomposition and corresponded to the N-benzoyl derivative of β-mononitrophenyl-β-alanine.

Found %: N 9.01, 8.92. $C_{16}H_{14}O_5N_2$. Calculated %: N 8.91.

A melting point test mixture with a sample of N-benzoyl-β-4-nitrophenyl-β-alanine (m. p. 181-183°), prepared by benzoylation of the corresponding nitroamino acid, decomposed at the same temperature. A slight melting point depression is due, evidently, to the difficulty of removing the unnitrated product.

N-Carbomethoxy-β-phenyl-β-alanine. 18 ml (22 g, 0.23 mole) methyl chlorocarbonate was added drop-wise, with stirring and at −2 to +1°, to a cooled solution of 30 g (0.18 mole) β-phenyl-β-alanine in 306 ml 10% caustic soda solution and the reaction mass was stirred for 1 hour at room temperature and acidified with hydrochloric acid (1:2) (Congo). The oil that came down crystallized upon standing. Yield 26.5 g (65.5%); m. p. 135-136°. Recrystallization from glacial acetic acid did not change the melting point.

Found %: C 59.02, 59.00; H 6.01, 5.91; N 6.52, 6.56. $C_{11}H_{13}O_4N$. Calculated %: C 59.15; H 5.88; N 6.28.

Nitration of N-carbomethoxy-β-phenyl-β-alanine. a) 3.8 ml (5.7 g, 0.09 mole) nitric acid (d 1.51) was added gradually, with stirring, to a suspension, cooled to 0°, of 10 g (0.045 mole) carbomethoxy derivative in 14 ml sulfuric acid (d 1.84) at such a rate that the temperature did not exceed 17°. The mixture was stirred for still some time and poured on ice. The oil that came down crystallized overnight. The crude product was purified by recrystallization from aqueous alcohol to which activated carbon was added. Yield 3.43 g (about 30 %); m. p. 152-154°. After recrystallization from ethyl acetate, the substance melted at 159-160°.

Found %: C 49.29, 49.25; H 5.28, 5.14. $C_{13}H_{12}O_6N_2$. Calculated %: C 49.23; H 4.52.

b) 3 ml (4.6 g, 0.07 mole) nitric acid (d 1.5) was added drop-wise with stirring at room temperature to a solution of 8 g (0.027 mole) carbomethoxy derivative in 50 ml glacial acetic acid. The mixture was stirred for a half hour more and heated for a half hour on a water bath (at 80°); further heating was stopped due to the formation of nitrogen oxides. Upon cooling, crystals came down (5.2 g) which had the same melting point as the initial substance and gave no melting point depression in a mixture test.

c) A nitrating mixture of 5 ml sulfuric acid (d 1.84) and 4.8 ml (7.4 g, 0.12 mole) nitric acid (d 1.5) was gradually added with stirring at 20-30° to a suspension of 13 g (0.044 mole) N-carbomethoxy-β-phenyl-β-alanine in 25 ml glacial acetic acid; the carbomethoxy derivative completely dissolved. The reaction mixture was stirred for 15 minutes more and poured on ice. The precipitate (11.1 g) was washed well with water and dried. M. p. 130-132°. There was no melting point depression of a test mixture with the initial substance.

N-Acetyl-β-phenyl-β-alanine. 20 ml (20 g, 0.19 mole) acetic anhydride was added drop-wise with stirring at 6-10° to a solution of 20 g (0.12 mole) β-phenyl-β-alanine and 23 g caustic soda in 200 ml water and the mixture was stirred for an hour more until the odor of the anhydride disappeared and then acidified with hydrochloric acid (1: 2). Yield 22 g (90.8%). M. p. 160-162° [7].

Nitration of N-acetyl-β-phenyl-β-alanine. 6.7 ml (10.22 g, 0.15 mole) nitric acid (d 1.51) was gradually added with stirring at 0-5° to a mixture, cooled to 0°, of 28 g (0.13 mole) acetyl derivative and 45 ml sulfuric acid (d 1.84); the reaction mixture was stirred for 1 hour at room temperature and poured on ice. The resinous substance which came down rapidly crystallized. Yield 28.5 g, m. p. 186° (with decomp.). Recrystallization from water yielded 20.5 g (60%) mononitro product with m. p. 205-206° (with decomp.).

Found %: N 10.96, 10.90. $C_{11}H_{12}O_5N_2$. Calculated %: N 11.11.

2.6 g pure substance was oxidized with 7.5 g potassium permanganate in 90 ml water and treated as described above. Isolated 0.9 g p-nitrobenzoic acid (80% of supposed mixture of nitrobenzoic acids); no other products were detected.

Ethyl ester of N-acetyl-β-4-nitrophenyl-β-alanine was prepared by treatment of the acylamino acid successively with thionyl chloride and alcohol. Yield 82%, m. p. 123-124.5° (from benzene).

Found %: N 9.83, 9.96. $C_{13}H_{16}O_5N_2$. Calculated %: N 10.11.

β-4-Nitrophenyl-β-alanine. 10 g (0.04 mole) N-acetyl-β-4-nitrophenyl-β-alanine was boiled for 2 hours with 60 ml hydrochloric acid (1: 1). Upon cooling, we obtained 8.2 g substance with m. p. 218-220° (with decomp.). Analysis proved it to be the hydrochloride of the desired nitroamino acid. Yield 84%.

Found %: N 11.58, 11.40. $C_9H_{10}O_4N_2 \cdot HCl$. Calculated %: N 11.36.

The free amino acid was obtained by treating the hot solution of the hydrochloride with a saturated solution of sodium acetate until there was no acid reaction on Congo. Yield 90%, based on the hydrochloride and 75% on the acetyl derivative. After recrystallization from 30% aqueous alcohol, β-4-nitrophenyl-β-alanine had m. p. 220-226° (with decomp.) Posner gives m. p. 226° [2].

Found %: N 13.62, 13.50. $C_9H_{10}O_4N_2$. Calculated %: N 13.35.

The N-benzoyl derivative was obtained by benzoylation of the given amino acid (Schotten-Baumann). Yield 75%. M. p. 181-183° (from dilute acetic acid).

Found %: N 8.62, 8.74. $C_{16}H_{14}O_5N_2$. Calculated %: N 8.91.

β-4-Nitrophenyl-β-ureidopropionic acid. A mixture of 2.1 g (0.01 mole) β-4-nitrophenyl-β-alanine and 8 g (0.13 mole) urea in 45 ml water was boiled for 15 hours on a water bath, then several milliliters of 4% aqueous alkali was added to the hot solution; it was then cooled and acidified with hydrochloric acid (1:3) (Congo). The yellow crystals which came down upon rubbing with a rod were separated and washed with water and alcohol. Yield 1.95 g β-ureido acid with m. p. 180° (with frothing). After recrystallization from 50% aqueous alcohol, the melting point was unchanged.

Found %: N 16.73, 16.51. $C_{10}H_{11}O_5N_3$. Calculated %: N 16.60.

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Upon boiling 1.2 g ureidoacid with 10 ml concentrated hydrochloric acid, 1 g of substance was obtained which melted at 238-240° with decomposition and corresponded in composition to 4-(4'-nitrophenyl)-dihydrouracil.

Found %: N 18.00, 17.88. $C_{10}H_9O_4N_3$. Calculated %: N 17.87.

SUMMARY

1. The nitration of β-phenyl-β-alanine was studied and it was shown that here a mixture of β-4-nitrophenyl-β-alanine and β-3-nitrophenyl-β-alanine is obtained, in which connection the first compound is formed in predominant amount.

2. The nitration of N-acyl derivatives of β-phenyl-β-alanine was studied and it was shown that they are converted in good yields into the corresponding N-acyl derivatives of N-acyl-β-nitrophenyl-β-alanine. On the example of N-acetyl-β-phenyl-β-alanine it was shown that the nitro group enters at the para- position to the side chain.

3. A preparative method for obtaining β-4-nitrophenyl-β-alanine was developed, and the compound was characterized by the preparation of a number of derivatives.

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BEHAVIOR OF DIPHENYL- AND TRIPHENYLAMINES TOWARD OXIDIZING AGENTS. X.

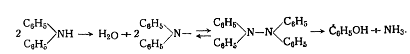
V. S. Smirnov

In a series of studies made by N. Ya. Demyanov and coworkers [1] the opinion was expressed that the direction of the oxidation process depends on the nature of the amine, the temperature, the reaction medium, and especially the nature of the oxidizing agent. As was established, the oxidation process, once it has started, passes through a number of intermediate phases to the final products. Frequently it is impossible to isolate the intermediate products.

For many years the author and coworkers, have studied the behavior of polymethylene and aliphatic amines toward various oxidizing agents [2], and a number of ways have been found to experimentally prove the theories expressed by N. Ya. Demyanov [3] on variation in the reaction medium, surface tension and viscosity in the process for the oxidation of amines.

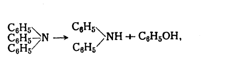
Wieland established in 1911 [4] that tetraphenylhydrazine (m. p. 147° with decomposition) is formed in the careful oxidation of diphenylamine with potassium permanganate in acetone solution. This compound gives colorless solutions in the cold. If a solution of tetraphenylhydrazine in toluene is heated to 70°, it acquires a greenish-brown color, ascribed to free radical formation. The color vanishes in the cold, and the starting tetraphenylhydrazine can be isolated from the solution.

In this communication we followed the transformations of diphenyl- and triphenylamines in concentrated sulfuric acid solution. The process for the transformation of diphenylamine in sulfuric acid solution probably proceeds by Scheme (1):



(1)

The process for the transformation of triphenylamine when it is oxidized in the presence of sulfuric acid proceeds by Scheme (2):



(2)

and then by Scheme (1).

EXPERIMENTAL

Oxidation of Diphenylamine. a) With hydrogen peroxide. 25 g diphenylamine was dissolved in 60 ml H_2SO_4 (d 1.84) and the flask was then fitted with a reflux condenser and the apparatus was placed on a water bath.

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Perhydrol (100 ml) was added to the solution in small portions in the course of 64 hours of heating. The oxidation proceeded smoothly. A black precipitate formed which was filtered off. The sulfuric acid anion was removed in the filtrate with saturated barium chloride solution. A small quantity of the filtrate was treated with alkali and an odor of ammonia was noted. The other part of the filtrate was treated with Nessler's reagent. The characteristic orange coloration appeared and a red-brown precipitate came down. The black precipitate was repeatedly treated with hot water on a filter. The sulfuric acid anion was removed. The solution was steamed down to low bulk. Upon standing, crystalline phenol (0.34-0.49 g) came down which with ferric chloride gave a violet coloration and also the Meltzer reaction and the reaction with Millon's reagent. A parallel experiment gave similar results.

b) With potassium permanganate. 25 g diphenylamine was dissolved in 60 ml H_2SO_4 (d 1.84) and the flask was fitted with a reflux condenser. Heating on a water bath was continued for 64 hours. 50 g $KMnO_4$ was added in small portions. 100 ml water was added. The resulting black precipitate was filtered off. The sulfuric acid anion was removed from the filtrate with saturated barium chloride solution. Ammonia was detected by the action of alkali and Nessler's reagent on the filtrate. The black precipitate was repeatedly treated with small portions of hot water. The sulfuric acid anion was removed from the solution with a saturated solution of barium chloride and the solution was steamed down to low bulk. Yield phenol (0.3-0.5 g), gave the characteristic qualitative reactions with ferric chloride, and the Meltzer and Millon reactions. A parallel experiment gave similar results.

Triphenylamine was synthesized from iodobenzene and diphenylamine by prolonged boiling with potash solution and powdered copper. M. p. ~ 126.8° after recrystallization from diethyl ether. After treatment with sulfuric acid and sodium nitrite and upon fusion with oxalic acid, it gave blue dyes of unknown structure.

Oxidation of triphenylamine. a) With hydrogen peroxide. 30 ml H_2SO_4 (d 1.84) was added to 10 g triphenylamine, dissolved in 50 ml acetone. The reaction conditions and treatment of products were the same as those described for the oxidation of diphenylamine. Ammonia and phenol (0.22-0.39 g) were obtained. Phenol gave marked qualitative reactions with ferric chloride, also the Meltzer and Millon reactions. A parallel experiment gave analogous results.

b) With potassium permanganate. 50 ml sulfuric acid (d 1.84) was added to 10 g triphenylamine, dissolved in acetone. The reaction conditions and treatment of products were analogous to those described for the oxidation of diphenylamine. Ammonia and phenol (0.39 g) were obtained. Phenol gave marked qualitative reactions. A parallel experiment gave analogous results.

SUMMARY

1. The oxidation of diphenylamine with hydrogen peroxide in sulfuric acid solution yields phenol and ammonia. The presence of tetraphenylhydrazine in the oxidation products could not be shown.

2. The oxidation of triphenylamine with either hydrogen peroxide or potassium permanganate in acetone solution, with the addition of sulfuric acid, yields phenol and ammonia.

3. The process for the transformation of diphenyl- and triphenylamines in their oxidation in sulfuric acid solution, judging from the final oxidation products, is comparable to the diazotization reaction for aniline; the difference consists only in the form of the cleaved nitrogen.

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BEHAVIOR OF CYCLOHEXANONE AZINE AND PHENYLHYDRAZONE TOWARD OXIDIZING AGENTS. XI.

V. S. Smirnov

In the oxidation of cyclohexylamine in the presence of copper [1] it was established that oxidative deamination takes place through the corresponding hydroxyamine stage. In the oxidation of cyclohexanone oxime with either hydrogen peroxide or potassium permanganate [2] it was established that a similar mechanism prevails for the transformation of the oxime. To establish the mechanism for the oxidation of polymethylene amines it appeared desirable to trace the behavior of other nitrogen-containing cyclohexanone derivatives so as to have a more complete picture of the transformations shown by this group of nitrogen compounds.

The process for the transformation of the azine and phenylhydrazone probably proceeds in the following manner:

$$C_6H_{10}{=}N{-}N{=}C_6H_{10} \rightarrow C_6H_{10}O + NH_3,$$
$$C_6H_{10}{=}N{-}NH{-}C_6H_5 \rightarrow C_6H_5OH + C_6H_{10}O + NH_3.$$

EXPERIMENTAL

The azine of cyclohexanone was prepared by heating cyclohexanone with hydrazine hydrate in alcoholic solution [3]. The azine, recrystallized from ether, had m. p. 33-34.5°, as per literature data [3, 4].

Oxidation of azine of cyclohexanone. a) With hydrogen peroxide. 90 ml of perhydrol was added in separate portions to 11 g of the azine of cyclohexanone. Heating on a water bath was continued for 64 hours. The resulting solution was yellow and had a pungent unpleasant odor. Distillation yielded fractions: 1st, b. p. to 120°, 2nd, above 120°. The residue in the distilling flask gave off ammonia. Upon treatment with caustic soda, the 1st fraction gave off ammonia. Nessler's reagent brought down a red-brown precipitate. The 2nd fraction divided into two layers. The upper cyclohexanone layer was separated. Yield 0.4 g.

b) With potassium permanganate. An aqueous solution of potassium permanganate (30 g in 80 ml water) was added in separate portions to 11 g azine of cyclohexanone. 10 ml sulfuric acid was added. The experiment was carried out as described above. Nessler's reagent brought down a red-brown precipitate. The 2nd fraction divided into two layers. The upper layer yielded 0.52 g cyclohexanone. The semicarbazone was prepared, which after recrystallization from boiling alcohol, came down in the form of fine crystals, m. p. 163-166°, corresponding to the semicarbazone of cyclohexanone.

Oxidation of phenylhydrazone of cyclohexanone. a) With hydrogen peroxide. 14 g of the phenylhydrazone, dissolved in 60 ml toluene, was taken for the oxidation. 70 ml perhydrol was added. Heating was continued for 64 hours. Two layers formed in the reaction flask. The upper layer was separated. Toluene was driven off. Isolated 0.4 g cyclohexanone. After toluene was driven off, a great deal of resinous product remained in the flask which in its solid state was very difficult to pulverize mechanically. The resinous product was soluble in toluene. Treatment with hot water yielded a small quantity of phenol which gave marked reactions with ferric chloride and the Meltzer and Millon reactions. Treatment of the solid product with alkali caused ammonia to be given off.

b) With potassium permanganate. 14 g phenylhydrazone of cyclohexanone in solution of 60 ml toluene was taken for the oxidation. 30 g $KMnO_4$ was consumed; it was added in small portions in aqueous solution. Heating was for 64 hours. 10 ml sulfuric acid (d 1.84) was added. After oxidation was complete, the black precipitate was filtered off. The filtrate divided into two layers. 0.44 g cyclohexanone was separated as the upper layer. From it was prepared the semicarbazone which after recrystallization from boiling alcohol, came down in the form of fine crystals, m. p. 165-166°, corresponding to the semicarbazone of cyclohexanone. After toluene was driven off, the lower layer solidified into a hard resinous mass in which phenol and ammonia were detected.

SUMMARY

1. The oxidation of cyclohexanone azine with either hydrogen peroxide or potassium permanganate yields cyclohexanone and ammonia.

2. The oxidation of cyclohexanone phenylhydrazone with either hydrogen peroxide or potassium permanganate yields cyclohexanone, phenol and ammonia.

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FORMATION OF POLYAMIDE RESINS

V. PARTICIPATION OF POLYMERIZATION AND POLYCONDENSATION REACTIONS IN TRANSFORMATION OF ϵ-CAPROLACTAM INTO POLYMERS

A. S. Shpitalny

Earlier [1] we had concluded that 7-membered lactams are capable of being transformed into polymers, either by stepwise (hydrolytic) polymerization or as the result of polycondensation. From this conclusion it followed that under suitable conditions for the transformation of ϵ-caprolactam (for example, in the presence of water), where the formation of two functional groups in one molecule is possible, which would differ in their sign of polarity, both of these processes will proceed simultaneously. Since the mechanism of polyamide resin formation from monomers of diverse structure is a current discussion topic [2, 3], we considered it advisable for us to contribute some additional data, supporting the above described transformation scheme for ϵ-caprolactam. To obtain these data we made use of the experimental material on the transformation of ϵ-caprolactam into polymer, already adapted by us to admit [1, 4] of only one reaction, either polymerization or polycondensation, and also of a series of experiments on the formation of polymer from ϵ-caprolactam in the presence of variable amounts of water and for different lengths of time.

We studied the transformation of ϵ-caprolactam into polymer on the example of reacting adipic acid with ϵ-caprolactam. In contrast to the earlier experiments in this direction [1, 4], in the present

TABLE 1
Reaction of Adipic Acid With ϵ-Caprolactam

Molar ratio adipic acid: ϵ-caprolactam	Temperature	Duration of the process (in hours)	Amount of reacted ϵ-caprolactam (in %)	Molar ratio adipic acid: ϵ-caprolactam in the reaction products
5 : 100	220*	2	3.8	1 : 1
5 : 100	220	8	20.9	1 : 4
5 : 100	220	24	78.7	1 : 16
1 : 1	220	2	68	—
1 : 1	220	3	100	1 : 1

case we prepared polymers with a high molecular weight, and we also varied the length of reaction time.

The data in Table 1 show that the rate for the transformation of ϵ-caprolactam into its reaction product with adipic acid depends on the concentration of the latter in the reaction mass. Small amounts

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of adipic acid retard the reaction, while large amounts accelerate it. Thus, at 220° and a molar ratio adipic acid : ϵ-caprolactam of 5:100, even when the process is run for 24 hours, only 78.7 % of the caprolactam reacts, whereas with a reactant molar ratio of 1 : 1 three hours is sufficient for all of the caprolactam to react.

It is necessary to emphasize that reaction in these experiments was exclusively stepwise polymerization. The participation of even traces of moisture was excluded by keeping the starting reactants in a desiccator for a long time over phosphoric anhydride. Consequently, the appearance in the literature [2] of statements that organic acids, in the absence of water, "do not catalyze" the transformation of ϵ-caprolactam into polymer, should be regarded as being due to insufficient experimental data on the reactions of lactams with organic acids.

TABLE 2

Polycondensation Processes Proceeding at 220° with Polyamide Formation from ϵ-Aminocaproic Acid and Low-Molecular Intermediate Transformation Products of ϵ-Caprolactam into Polymer.

Starting products	Duration of process (in minutes)	M Polymer
Aminocaproic acid	15	1500 *
Ditto	30	4950
"	120	6400
Low-molecular polymers (M 3000)	30	6250
Ditto	60	15000

* Prior to molecular weight determination there was removed 10.6% of water-soluble products from the reaction mass by washing.

To keep the polycondensation and polymerization processes separate, the same as in earlier studies [1, 4], the intermediate transformation products of ϵ-caprolactam into polymer, being low-molecular polyamide polymers, were treated in suitable manner, in which connection the latter were completely freed from caprolactam and from water-soluble products by successive washing with benzene and with water. Here the transformation rate of these products into polymer was determined in comparison to the rate of polymer formation from ϵ-aminocaproic acid.

From the data in Table 2 it follows that the rate of the polycondensation process is exceedingly fast even at 220°, — it is much faster than the stepwise polymerization reaction. Since we were able to find only traces of the lactam in the transformation products, it must be assumed that participation of the polymerization reaction could not exert much influence on the obtained results.

From a comparison of both sets of experimental results it can be concluded that in the transformation of ϵ-caprolactam into polymer the bifunctional compounds that arise here (a mixture of monomers and low-molecular polymers) should very rapidly form polymers with higher molecular weight, and consequently the concentration of low-molecular polymers in the reaction mass should fail to be high at any moment in the process. At the same time any additions, facilitating an increase in the amount of functional groups in the reaction mass, will favor an increase in the reaction rate, and especially in the initial stage of the process.

The transformation of ϵ-caprolactam into polymer, as follows from an examination of the experiments on the formation of polymer in the presence of variable amounts of water and for different lengths of time, shows characteristics that are evoked by participation of both of the above-examined reactions (Table 3).

TABLE 3

Transformation of ϵ-Caprolactam into Polymer in the Presence of Variable Amounts of Water and for Different Lengths of Time

Experiment Nos.	Amount of water in the reaction mass		Duration of process (in hours)	Temperature	Amount of water insoluble polymers (in %)	M of water-insoluble polymer	Amount of water-soluble polymers (in %)	M of water-soluble polymers	Calculated * amount of aminocaproic acid (in %)
	Wt. %	Mole %							
1	2	11.1	2	220°	1.1	1660	1.1	400	1.56
2			3	220	50	3000	1.4	400	2.4
3			4	220	80	6000	1.78	400	2.2
4			5	220	87.7	7400	1.72	400	2.00
5	17	94.4	2	220	89.6	2850	5.17	400	5.3
6			3	220	90.4	3175	1.92	400	4.1
7			4	220	90.7	4000	1.80	400	3.0
8			5	220	93.6	4000	2.00	400	3.00
9	5	27.7	2	230	56.0	833	2.6	400	9
10			3	230	79.5	3333	5.2	400	4.5

* The amount of aminocaproic acid was calculated on the basis that the transformation of the lactam into polymer proceeds only by the usually recommended stepwise polymerization scheme [5], in accord with which each polymeric molecule can be formed with the aid of only one aminocaproic acid molecule.

The small amount of low-molecular fractions in the reaction mass, being observed during the whole process, appears, as was indicated above, quite regular and is explained by the more rapid rate of polycondensation reactions when compared with ring hydrolysis reactions.

An acceleration of the process with increased amounts of water in the reaction mass is also in accord with the conclusions made above, since in this case the amount of functional groups in the reaction mass increases, which facilitates the progress of both polymerization and polycondensation reactions.

And finally, if the amount of ϵ-caprolactam, subjected to hydrolysis by water, is judged by the amount of aminocaproic acid that will be formed if only the usually recommended polymerization scheme [5] is considered, then based on the data obtained for different stages of the process, this amount decreases toward the end of the process. Data of this character could have place only with participation of the polycondensation reaction in the process. If only the polymerization process is present, as is postulated at times [2], then the amount of aminocaproic acid, calculated in accord with the indicated method, should fail to show decrease toward the end of the process.

From the obtained data it follows that the scheme proposed by Carothers for the transformation of 6-membered lactones into polymers [6] can be applied to the corresponding transformations of 7-membered lactams, not fully, as we had done earlier [1], but with certain modifications, and namely:

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This scheme predicts the course of both the stepwise polymerization and the polycondensation processes. It differs from the above-mentioned scheme of Carothers in that the polymer is found in equilibrium, not with the starting monomer (in the present case with the lactam), but instead with a mixture of the starting monomer and low-molecular polymer.

EXPERIMENTAL

The reaction of adipic acid with ϵ-caprolactam was carried out the same as in the preceeding works [1, 4]. To determine the quantity of unreacted lactam, the melt was treated with benzene. The lactam passed into solution, the insoluble residue was filtered off, washed with benzene, dried, weighed and its molecular weight was determined by titration of the end groups. The quantity of lactam was established by determination of dry residue in the benzene extract.

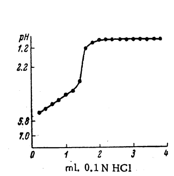

Figure 1

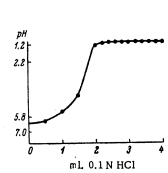

Figure 2

In the experiments on conversion of ϵ-aminocaproic acid to a polymer, the melt obtained by holding a weighed sample for a fixed interval of time at 220° in a sealed ampoule (from which air had been displaced by carbon dioxide) after treatment with benzene and drying, was extracted with hot water to remove the water-soluble polymers. In contrast to the preceeding experiments, in the given case only traces of lactam were detected in the benzene extract. In the same manner we treated the melt, obtained from low-molecular polymers – intermediate products formed by conversion of lactam to high-molecular polyamides and also the melts which were reaction products of ϵ-caprolactam and water.

The molecular weights of the water-soluble products were determined by potentiometric titration (glass electrode) of the amino groups of the polymer in phenol-methanol solution (Fig. 1) (2 volumes phenol + 1 volume methanol) [7] (found M 415) or by titration by the formol method [8] (found M 454, 400).

The molecular weights of the water-insoluble polymers were determined by potentiometric titration (Fig. 2) (found M 2400) or by titration of polymer solutions in benzyl alcohol at about 170° in the presence of phenolphthalein with 0.1 N KOH solution. The latter was prepared by solution of KOH in benzyl alcohol, containing 10% methyl alcohol [7] (found M 2353, 2850).

SUMMARY

1. Additional data were presented in support of the scheme for the transformation of ϵ-caprolactam into polymer in the presence of water, in which both the polycondensation and polymerization reactions participate: a) a low concentration of low-molecular polymers in the reaction mass during the whole process, b) an increase in the process rate with increase in the amount of water in the reaction mass, and c) a decrease in the number of functional groups in the reaction mass toward the end of the process.

2. The comparative rate of polycondensation and polymerization reactions was shown on the example of converting ϵ-caprolactam into polymer by each of these reactions separately. In this way it was established that polycondensation reactions proceed considerably faster than do stepwise polymerization reactions.

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REACTION OF MESITYLMAGNESIUM BROMIDE WITH THE ALLYL ESTERS OF TRIMETHYLACETIC AND FORMIC ACIDS

E. B. Sokolova and M. E. Dolgaya

One of the anomalous directions of the organomagnesium synthesis with participation of esters leads to the formation of hydrocarbon reaction products as the result of the alcohol residue (R') of the ester radical condensing with the radical (R") of the organomagnesium compound. Arnold and coworkers [1] on much experimental material showed that when phenylmagnesium bromide is used the cleavage of esters by the indicated scheme is observed if: 1) the radicals of the acidic residues create considerable steric hindrance, and 2) the radicals of the alcoholic residues show a tendency to form cations (as, for example, allyl, crotyl, etc.). According to the data of Arnold, Bank and Liggett (see [2]), ester cleavage with the formation of hydrocarbon products of the R' R" type fails to occur when allyl trimethylacetate is reacted with phenylmagnesium bromide. Since steric hindrance increase in the organomagnesium compound augments its ester cleavage action [3], in this study we decided to examine the cleavage action of mesitylmagnesium bromide on the allyl esters of trimethylacetic, acetic and formic acids, for which the above indicated type of cleavage reaction was not observed earlier.

As the result of our experiments it was established that allyl trimethylacetate is cleaved by mesitylmagnesium bromide to give cleavage products in 20% of the theoretical yield. Substitution of isobutenyl for the allyl radical increases the yield of cleavage reaction products to approximately 35%.

Allyl acetate and allyl formate, under the influence of mesitylmagnesium bromide, fail to form the R' R" type of hydrocarbon cleavage product. In the experiment with allyl formate the hydrocarbon obtained by us was dimesitylmethane. Its formation is evidence that in the given case, the same as in the reaction of ethyl formate with mesitylmagnesium bromide [4], reaction proceeds by the normal scheme. The reaction of mesitylmagnesium bromide with trimethylacetyl chloride gave tert-butyl mesityl ketone in up to 40% yield.

EXPERIMENTAL

Reaction of mesitylmagnesium bromide with allyl trimethylacetate. Allyl trimethylacetate, which was obtained in 70% yield by Spasov's method [5] from trimethylacetyl chloride and allyl alcohol, had the following properties: b. p. 138-142°, n_D^{20} 1.4119, d_{20}^{20} 0.8877. For the organomagnesium synthesis was taken: 100 g mesityl bromide, 12 g magnesium filings, 72 g allyl trimethylacetate.

The reaction product was heated on a water bath for 16 hours and decomposed with saturated NH_4Cl solution, acidified with HCl. The ethereal solution of reaction products was extracted three times with

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10% Na_2CO_3 solution. After the ether was removed the soda extracts were acidified with 20% H_2SO_4 and trimethylacetic acid was driven off together with water. 10 g trimethylacetic acid was obtained, corresponding to a 20% yield of cleavage reaction products. After ether was driven off, the reaction products were vacuum-distilled twice. 20 g low-boiling fraction with constant refractive index was treated with 10% NaOH solution for extraction of mesitol. The crystalline product separated from the alkaline layer upon acidification had a pungent phenolic odor and b. p. 67-68°, corresponding to mesitol. The properties of the mesitol reaction product freed from admixture were as follows:

B. p. 87-88° (5 mm), d_{20}^{20} 0.9065, n_D^{20} 1.5149, MR_D 53.22; Calc. 53.55.

Found %: C 89.54; H 10.70. $C_{12}H_{16}$. Calculated %: C 90.00; H 10.00.

Bromine numbers by Kaufman's method: 103.1 and 102.9. Since the molecular weight of allylmesitylene is 160, the bromine number was numerically equal to % of unsaturated products.

The analytical data presented indicate the product to be allylmesitylene.

Reaction of mesitylmagnesium bromide with isobutenyl trimethylacetate *. Preparation of isobutenyl trimethylacetate. Isobutenyl chloride [6] was hydrolyzed with aqueous potash solution by Sheshukov's method [7] until disappearance of the organic layer. After evaporation and dehydration of the distillate with calcined potash and anhydrous $CuSO_4$, isopropenylcarbinol with d_4^{20} 0.8572 was isolated. The ester of isopropenylcarbinol and trimethylacetic acid was prepared by addition of 0.6 mole of the acid chloride to a solution of 0.5 mole alcohol in mixture of anhydrous pyridine (1 mole) and absolute ether (150 ml) upon heating on a water bath. Yield of ester 90%.

B. p. 156-158° (750 mm), d_{20}^{20} 0.8750, n_D^{20} 1.4172, MR_D 44.84; Calc. 44.95.

For the organomagnesium synthesis we took 90 g mesityl bromide, 12 g magnesium, 70 g isobutenyl trimethylacetate. The reaction product was heated for 8 hours on a water bath and then treated the same as in the preceding synthesis. The total amount of trimethylacetic acid that separated out due to the cleavage reaction in this experiment was 16 g, i.e., 35% of amount of ester taken for the reaction. After the ether was driven off, the reaction product was given 2 vacuum-distillations and yielded 26 g narrow-boiling fraction. After treatment with 10% NaOH solution (to extract mesitol), the product distilled in the range 102-104° (6-7 mm).

d_{20}^{20} 0.9009, n_D^{20} 1.5123; MR_D 57.97; Calc. 58.16.

Found %: C 89.60; H 10.26. $C_{13}H_{18}$. Calculated %: C 89.65; H 10.35.

Bromine number by Kaufman's method: 104.2, Calc. 92.00.

Reaction of mesitylmagnesium bromide with trimethylacetyl chloride. For reaction we took 100 g mesityl bromide, 12 g magnesium, 60 g trimethylacetyl chloride. The mesitylmagnesium bromide solution was run into the ethereal acid chloride solution [8] and heating up was noted with the appearance of red coloration of the solution. The reaction product was heated on a water bath for 12 hours and then decomposed with 10% acetic acid solution. The ethereal solution was treated twice with 10% NaOH solution to remove free acid and mesitol, dried over calcined potash and distilled. Repeated distillations yielded about 40 g product, the main bulk of which distilled at 125-126° (8 mm).

d_{20}^{20} 0.9623, n_D^{20} 1.5040, MR_D 62.78; Calc. 63.26.

Found %: C 82.53; H 10.05. $C_{14}H_{20}O$. Calculated %: C 82.35; H 9.80.

* M. A. Golovanova participated.

The obtained ketone could not be identified through its semicarbazone. The available literature data states that due to steric hindrances, dimesityl ketone [9] and hexamethylacetone [10] also give no semicarbazone, oxime or phenylhydrazone type derivatives. The investigated ketone was therefore reduced to the corresponding carbinol with metallic sodium in boiling ethyl alcohol [9] two-fold reduction converted the ketone to carbinol only to the extent of 56% (found %: OH 4.65; calc. 8.25). The reduced ketone distilled at 145-147° (10 mm) and was of viscous consistency. The freshly distilled product had d_{20}^{20} 0.9781 and n_D^{20} 1.5137. The reduced ketone crystallized upon standing. The pressed off crystals were twice recrystallized from dilute ethyl alcohol; m. p. 35-36°.

Found %: C 81.69; H 10.30. $C_{14}H_{22}O$. Calculated %: C 81.56; H 10.68.

The carbinol was identified through the benzoyl derivative obtained by reaction of benzoyl chloride with solution of the substance in a mixture of pyridine and chloroform with heating on a water bath [11]. The benzoyl derivative was recrystallized from petroleum ether and twice recrystallized from dilute ethyl alcohol, after which it had m. p. 81-82°.

Found %: C 81.48; H 8.42. $C_{21}H_{26}O_2$. Calculated %: C 81.29; H 8.29.

Reaction of mesitylmagnesium bromide with allyl formate. Allyl formate was prepared from anhydrous oxalic acid and anhydrous glycerol by method described in [12]. We took 40 g mesitylene bromide, 6 g magnesium, 18 g allyl formate; addition of the latter to a solution of mesitylmagnesium bromide caused a crimson coloration which turned brown. The reaction product was decomposed with 10% acetic acid. After distillation of the fractions which came over up to 200° at atmospheric pressure, the residue was vacuum-distilled. The temperature of the vapors quickly rose to 188-190° (6 mm); at this point about 3 g of product, m. p. 134°, crystallized in the outlet tube of the flask and in the condenser. The residue in the flask solidified into a hard vitreous mass, insoluble in ethyl alcohol but readily soluble in benzene, acetone and in petroleum ether. Evidently, the residue was a linear polymer of allyl formate. Percentage analysis showed the resulting crystalline product to be dimesitylmethane.

Found %: C 90.24; H 9.92. $C_{19}H_{24}$. Calculated %: C 90.56; H 9.44.

SUMMARY

1. It was shown that allyl trimethylacetate is cleaved to the extent of 20% when it is reacted with mesitylmagnesium bromide. Replacement of the ester allyl radical by isobutenyl increases the yield of cleavage products to 35%.

2. Allyl formate reacts with mesitylmagnesium bromide by the normal scheme to yield dimesitylmethane.

3. The reaction of mesitylmagnesium bromide with trimethylacetyl chloride gave tert-butyl mesityl ketone, which can be converted into the corresponding carbinol by sodium reduction in alcohol medium.

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STRUCTURE OF CHLOROPHENOXYCROTONIC ACIDS

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Julia and Tchernoff [1] described the preparation of chlorophenoxycrotonic acids, where the melting points of the acids obtained by these authors strongly differed from the constants of the substances that we had synthesized earlier by other methods [2]. In connection with this we ran the oxidative cleavage of two different acid specimens for the purpose of establishing the position of the double bond. The oxidation was run by the gradual addition of 2% potassium permanganate solution to a known weight of the acid dissolved in 1% soda solution. Oxidation of the acid, synthesized by the method of the French authors, gave the expected chlorophenoxyacetic acid, while oxidation of the acid obtained by our method [2] gave chlorophenol, identified as the benzoyl derivative. Consequently, it must be assumed that in our published paper [2] we failed to obtain the chlorophenoxycrotonic acids, and instead we obtained the corresponding chlorophenoxyvinylacetic acids: the p-chloro-, 2, 4-dichloro- and 2, 5-dichlorophenoxyvinylacetic acids.

EXPERIMENTAL

2, 4-Dichlorophenoxycrotonic acid (m. p. 186-187°) [1]. A 2% solution of potassium permanganate (110 ml) was added drop-wise to a solution of the above acid in 150 ml 1% soda solution until a pink coloration was obtained. Manganese dioxide was filtered off and the filtrate was steamed down to 50 ml volume. On cooling, the solution was acidified with hydrochloric acid (Congo) and an oil formed which solidified upon standing. The solid product was separated, washed with water and dried in a desiccator. Weight 0.65 g (80%); m. p. 137-138° (from water). The substance gave no melting point depression in mixture with 2, 4-dichlorophenoxyacetic acid.

Acid with m. p. 112-113° [2]. A solution of 1.06 g acid in 150 ml 1% soda solution was oxidized with a solution of 1.8 g potassium permanganate in 90 ml water. Manganese dioxide was filtered off and the filtrate was steamed down to 30 ml volume. On cooling, the solution was again filtered and then acidified with 5% sulfuric acid (Congo); a small quantity of substance separated out which had the characteristic odor of 2, 4-dichlorophenol. The acidic solution was treated with ether. The solvent was driven off from the ethereal extracts and the residue was dissolved in 10% caustic potash solution and shaken with benzoyl chloride. The resulting precipitate of the benzoyl derivative was separated, washed with water and dried in a desiccator. Weight 0.65 g (60%); m. p. 94-95.5° (from aqueous alcohol). The melting point of the benzoyl derivative of 2, 4-dichlorophenol was 96° [3]. When the permanganate solution was added until a rose coloration appeared in the oxidation reaction, a considerable amount of solution is consumed and further treatment yielded only resinous products which probably result from the oxidation of dichlorophenol.

SUMMARY

It was established that the products obtained in the reaction of sodium chlorophenolates with γ-bromocrotonic ester, followed by saponification, appear as chlorophenoxyvinylacetic acids, and not as chlorophenoxycrotonic acids, as we had postulated earlier.

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HIGH-MOLECULAR COMPOUNDS

XCIII. PROPERTIES OF THE POLYESTERS OF TETRAMETHYLENE GLYCOL AND 1,3-BUTANEDIOL

V. V. Korshak and S. V. Vinogradova

In previous communications we have presented data on the polyesters of ethylene glycol, hexamethylene glycol, decamethylene glycol, eicosamethylene glycol, propylene glycol, diethylene glycol and triethylene glycol with dicarboxylic acids of general formula $HOOC(CH_2)_n COOH$, with n ranging from 0 to 8, and the dependence of the properties of these polyesters on their structure was examined [1-5]. In this communication we give our investigation results on the polyesters of tetramethylene glycol and 1,3-butanediol with various dicarboxylic acids. The method used to obtain the polyesters was the same as that described earlier [2, 4]. For the polymers obtained in this manner we determined the melting points, the transition temperatures into the visco-liquid state, the flow points, the solubilities in benzene and alcohol, and the specific viscosities of 0.5% benzene solutions. The melting points of the solid polymers were determined in capillary tubes, and those of the liquid polymers in test tubes (freezing in a mixture of dry ice and acetone). The flow points and temperatures of transition into the visco-liquid state were determined in a Höppler consistometer under a load of 1 kg. For the solubility determinations a weighed sample of the polyester, known to be insoluble in the given amount of solvent, was placed in a flask fitted with reflux condenser, and heated for 3 hours at solvent boil. For the alcohol solubility determinations a 0.5 g sample of the polyester and 10 ml of alcohol were taken. On conclusion of heating the solution was cooled to room temperature, the polymer portion failing to dissolve was filtered, the determined filtrate volumes were placed in cuvettes, the solvent evaporated, and the solubility of the polyester in grams per liter was calculated from the residue weight. The viscosimetric method was used to calculate the molecular weights of the polyesters, taking $K = 0.93 \cdot 10^{-4}$ for benzene and $1.75 \cdot 10^{-4}$ for cresol. The results obtained by us are given in Table 1.

The dependence of the melting points of the tetramethylene glycol polyesters on the number of carbon atoms in the molecule of the starting dicarboxylic acid is shown in Fig. 1.

Similar to the polyesters of other polymethylene glycols previously studied by us, the variation in the melting points of the tetramethylene glycol polyesters as a function of the number of carbon atoms in the acid molecule assumes the form of a zigzag line. The polyesters, obtained from dicarboxylic acids containing an even number of carbon atoms in the molecule, melt higher than do the polyesters, obtained from dicarbozylic acids that contain and odd number of carbon atoms in the molecule. The highest melting point (113-114°) is shown by the polyester of tetramethylene glycol and succinic acid. The lowest melting point in the series of polyesters prepared from tetramethylene glycol and dicarboxlyic acids with an even number of carbon atoms in the molecule is observed for the polyester of adipic acid (57°), after which the polyester melting points rise in measure with increase in the length of the methylene chain in the starting dicarboxylic acid. The lowest melting point in the series of polyesters prepared from dicarboxylic acids with an odd number of carbon atoms in the molecule is observed for the polyester of malonic acid, being a viscous liquid with m.p. -22°. In measure with increase in the length of the methylene chain in the series of polyesters prepared from dicarboxylic acids with an odd number of carbon atoms in the molecule a rise in the melting points of the polyesters obtained from them is observed. Thus, the polyester of glutaric acid is a solid with m.p. 36°, polytetramethylene pimelate melts at 38°, and polytetramethylene azelate melts at 49°.

A study of some of the polyesters with the aid of the consistometer revealed that the character of the changes in the flow points and in the transition points into the visco-liquid state as a function of the number of carbon atoms in the molecule of the starting acid was similar to that shown by the changes in the melting points of the polyesters. The polyesters, obtained from oxalic, adipic and sebacic acids, i. e. from acids containing an even number of carbon atoms in their molecule, show higher values for the given constants

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TABLE 1

Expt. Nos.	Polyester	Melting point		Flow Point	Transition point into the visco-liquid state	Solubility in alcohol (g/liter)	Specific viscosity of a 0.5% polymer solution		Molecular weight
		Not purified	Purified				in benzene	in cresol	
1	$-CO-CO-O(CH_2)_4O-$	103—105°	—	—	—	1.55	—	0.1	2060
2	$-CO-CO-O(CH_2)_4O-$	103—104	—	102°	94°	—	—	0.245	5040
3	$-COCH_2CO-O(CH_2)_4O-$	—24 ÷ —20	—	—	—	4.62	0.07	—	2570
4	$-COCH_2CO-O(CH_2)_4O-$	—22 ÷ —17	—	—	—	—	—	0.23	4620
5	$-COCH_2CH_2COO(CH_2)_4O-$	113—114	113—114	—	—	—	—	—	—
6	$-COCH_2CH_2COO(CH_2)_4O-$	113—114	—	—	—	1.75	—	0.19	3730
7	$-CO(CH_2)_3CO-O(CH_2)_4O-$	36—38	—	40	38	5.55	0.1	—	3630
8	$-CO(CH_2)_4CO-O(CH_2)_4O-$	58—60	58—60	61	60	—	0.08	0.17	2850
9	$-CO(CH_2)_4CO-O(CH_2)_4O-$	57—60	58—60	—	—	3.55	0.11	—	3920
10	$-CO(CH_2)_5CO-O(CH_2)_4O-$	38—41	—	43	42	7.27	0.1	—	3530
11	$-CO(CH_2)_7CO-O(CH_2)_4O-$	49—51	49—51	51	43	4.62	0.09	—	3120
12	$-CO(CH_2)_8COO(CH_2)_4O-$	64—67	—	—	—	—	0.11	0.2	3780
13	$-CO(CH_2)_8COO(CH_2)_4O-$	65—67	65—67	69	68	1.63	0.12	—	4130
14	$-CO-CO-OCH_2CH_2CH(CH_3)O-$	—4 ÷ —2	—	—	—	34.9	0.028	—	1220
15	$-CO-CO-OCH_2CH_2CH(CH_3)O-$	—6 ÷ —1	—	—	—	—	0.025		1100
16	$-COCH_2COOCH_2CH_2-CH(CH_3)O-$	—20 ÷ —17	—	—	—	—	0.025		1100
17	$-COCH_2COOCH_2CH_2-CH(CH_3)O-$	—20 ÷ —17	—	—	—	28.9	0.03		1250
18	$-CO(CH_2)_2COOCH_2CH_2CH(CH_3)O-$	—15 ÷ —11	—	—	—	24	0.036		1480
19	$-CO(CH_2)_3COOCH_2CH_2CH(CH_3)O-$	—32 ÷ —28	—	—	—	77.25	0.016		640
20	$-CO(CH_2)_3COOCH_2CH_2CH(CH_3)O-$	—36 ÷ —33	—	—	—	—	0.05		2000
21	$-CO(CH_2)_4COOCH_2CH_2CH(CH_3)O-$	—36 ÷ —34	—	—	—	—	0.039		1500
22	$-CO(CH_2)_5COOCH_2CH_2CH(CH_3)O-$	—43 ÷ —39	—	—	—	—	0.031		1200
23	$-CO(CH_2)_7COOCH_2CH_2CH(CH_3)O-$	—52 ÷ —48	—	—	—	—	0.032		1200
24	$-CO(CH_2)_8COOCH_2CH_2CH(CH_3)O-$	—44 ÷ —41	—	—	—	69.3	0.047		1700
25	$-CO(CH_2)_{10}COOCH_2CH_2(CH_3)O-$	—12 — —10	—	—	—	—	—		—

than do the polyesters, obtained from glutaric, pimelic and azelaic acids. Also characteristic is the fact that the transition from the visco-liquid state to the fluid state takes place in a short temperature interval. Thus, for polytetramethylene glutarate this interval is 2°, and for polytetramethylene pimelate, polytetramethylene adipate and polytetramethylene sebacate it is 1°; this interval is somewhat greater for the polyesters of oxalic and azelaic acids, being 8°. The short temperature interval for the transition from the visco-liquid into the fluid state indicates that the given polyesters are crystalline substance. In two cases (2 and 4 in Table 1) for the tetramethylene glycol polyesters the polycondensation was run in the presence of a catalyst — lithium hydroxide, taken in an amount equal to 0.25% of the diethyl oxalate (or diethyl malonate) weight, for the purpose of obtaining polyesters with a somewhat higher specific viscosity, i. e. with a higher molecular weight. The melting points of the polyesters obtained here either completely failed to differ from the melting points of the polymers obtained in the absence of catalyst (1 and 2), or they differed very slightly (-24° for 3 and -22° for 4), although the specific viscosities of these polymers, for example, for 1 and 3, showed a 2.5-fold change (0.1 for 1, and 0.245 for 2). This fact indicates that the variations in the molecular weights, which exist for the polyesters obtained by us, fail to exert much influence on their melting points. The latter is very clearly seen if we compare (among themselves) the melting points of the polyethylene sebacates with different molecular weights, given in Table 2.

Different polyethylene sebacate specimens with the specific viscosities of their 0.5% benzene solutions ranging from 0.17 to 9.65 show practically no variation in their melting points. This gives us basis to assume comparab... melting points for the polyesters of different acids and glycols, despite the variations prevailing in their molecular weights. The method developed by us for the preparation of polyesters is such that in the last stage of the process the polymer is heated in vacuo to quite high temperatures (250°). This permits assuming that the polymer, obtained as the reaction result, will fail to contain any low-molecular impurities (in its composition),

TABLE 2

Specific viscosity of a 0.5% benzene solution of polyethylene sebacate	Melting point of the polyethylene sebacate
0.17	75-76°
0.18	76-78
0.19	76-79
0.21	77-78
0.28	76-79
0.45	78-81
0.45	79-81
0.65	76-78

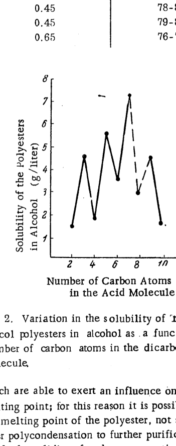

Fig. 2. Variation in the solubility of tetramethylene glycol polyesters in alcohol as a function of the number of carbon atoms in the dicarboxylic acid molecule.

which are able to exert an influence on its melting point; for this reason it is possible to determine the melting point of the polyester, not subjecting it after polycondensation to further purification. To verify the validity of such an assumption we subjected some of the tetramethylene glycol polyester specimens (5, 9, 8, 11 and 13, Table 1), obtained after polycondensation, to purification — to a double precipitation with petroleum ether from their benzene solutions; the melting points of the specimens purified in this manner proved to be practically the same as those of the polyesters that had not been subjected to additional purification.

The alcohol solubility of the tetramethylene glycol polyesters was also determined. The variation in the alcohol solubility as a function of the number of carbon atoms in the starting dicarboxylic acid is shown by the broken line (Fig. 2). From the graph it can be seen that the solubility of the polyesters in alcohol changes in direct opposition to the changes in the melting points;

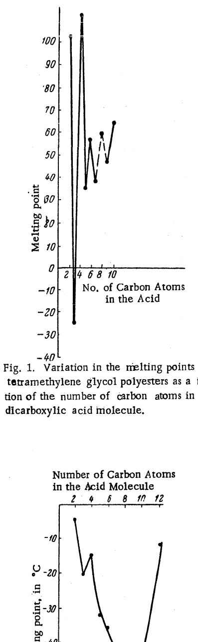

Fig. 1. Variation in the melting points of tetramethylene glycol polyesters as a function of the number of carbon atoms in the dicarboxylic acid molecule.

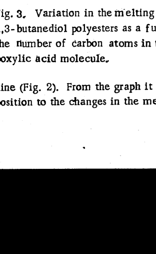

Fig. 3. Variation in the melting points of 1,3-butanediol polyesters as a function of the number of carbon atoms in the dicarboxylic acid molecule.

the greatest solubility is shown by the polyesters that were obtained from dicarboxylic acids with an odd number of carbon atoms in their molecule. The alcohol solubility of the tetramethylene glycol polyesters is slight and ranges from 1.55 to 7.27 g/liter. The given polyesters show much better solubility in benzene. Thus, a 2 g sample of polytetramethylene adipate, and 1.5 g samples each of polytetramethylene sebacate and polytetramethylene malonate, are completely soluble in 5 ml of benzene. Data on the polyesters obtained from the isomeric glycol, namely 1,3-butanediol, are also given in Table 1. Data on the polyesters of propylene glycol has already been published by us [3]. On this example was shown the great influence exerted by the methyl group on polyester properties. It seemed of interest to confirm our earlier obtained data and to verify them on the example of another gylcol, having a sidechain methyl group. For this purpose we synthesized some 1,3-butanediol polyesters, which also had interest from the viewpoint of studying the properties of polyesters with an odd number of methylene groups in the glycol chain. As can be seen from the data shown in Table 1 and Fig. 3, where the curve showing the relationship between variation in the melting points of 1,3-butanediol polyesters and the number of carbon atoms in the dicarboxylic acid molecule is given, a change in the positions of the hydroxyl groups in the butanediol produces considerable change in the properties of the obtained polymers. The whole curve for the melting point variations of the polyesters obtained from 1,3-butanediol and the investigated acids lies in the region of negative melting points, whereas in the case of the tetramethylene glycol polyesters only the malonic acid polyester was liquid. Also characteristicfor the polyesters of 1,3-butanediol is the fact that the zigzag character of the curve showing variation in the melting points of polyesters is in the main upset, being retained only for the first three members of the homologous series: the polyesters of oxalic, malonic and succinic acid. Beginning with the polyester of 1,3-butanediol and succinic acid, an increase in the methylene groups of the starting dicarboxylic acid produces a gradual reduction in the polyester melting points clear up to the polyester of azelaic acid, which possesses the lowest melting point of all of the polyesters in this series (-52°). Further increase in the length of the hydrocarbon chain in the dicarboxylic acid leads to an increase in the polyester melting points; thus, the polyester of sebacic acid already melts at -44°, and that of decanedicarboxylic acid at -12°. A comparison of these data with the data obtained for the propylene glycol polyesters, reveals that the character of the curve showing melting point variation as a function of the number of carbon atoms in the dicarboxylic acid molecule is the same for these two types of polyesters. However, it is necessary to mention that an increase of one methylene group (from two to three) in the hydrocarbon chain of the starting glycol leads to the situation that 1,3-butanediol polyesters show lower melting points than do the corresponding propylene glycol polyesters. As a result, a side methyl group is a very effective internal plasticizer, neutralizing the influence of the eveness factor of the dicarboxylic acid, for a difference in the melting points of polyester obtained from even- and odd-numbered dicarboxylic acids is absent over a large portion of the melting point curve. The strong plasticizing influence exerted by a side methyl group is further shown in the fact that clear up to the polyester of azelaic acid the melting points of the polyesters decrease in measure with the accumulation of methylene groups in the starting dicarboxylic acid, and also in that the polymers appear as liquids with very low melting points. Determination of the alcohol solubilities of the given polyesters revealed that they are much more soluble than the tetramethylene glycol polyesters. Especially good solubility is shown by the polyesters of 1,3-butanediol with adipic, pimelic and azelaic acids. The polyesters of oxalic, malonic and succinic acid are less soluble.

SUMMARY

1. The polyesters of tetramethylene glycol and of 1,3-butanediol with oxalic, malonic, succinic, adipic, glutaric, pimelic, azelaic, sebacic and decanedicarboxylic acids were prepared.

2. It was shown that the polyesters of tetramethylene glycol and dicarboxylic acids with an even number of carbon atoms in the molecule melt higher than do the polyesters of dicarboxylic acids with an odd number of carbon atoms in the molecule.

3. On the polyesters of 1,3-butanediol it was shown that the introduction of a side methyl group in the polyester molecule sharply lowers their melting points.

4. On the example of polyethylene sebacate, polytetramethylene oxalate and polytetramethylene malonate,it was established that the melting points of polyesters of different molecular weight differ but slightly among themselves.

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HIGH-MOLECULAR COMPOUNDS

XCIV. POLYESTERS OF TRIMETHYLENE AND PENTAMETHYLENE GLYCOLS

V. V. Korshak and S. V. Vinogradova

In previous communications [1-6] we have shown that the properties of polyesters are substantially influenced by both the total number of carbon atoms in the molecule of the starting dicarboxylic acid and by whether this number is either odd or even. The polyesters of even-numbered polymethylene glycols, obtained from dicarboxylic acids also with an even number of carbon atoms in the molecule, showed higher melting points than did the polyesters of dicarboxylic acids with an odd number of carbon atoms in the molecule. The question of whether an even or odd number of methylene groups in the molecule of the starting glycol exerts an influence on the melting point of the polymer has failed to receive an exhaustive answer.

As study subjects for the purpose of elucidating this question we took the polyesters of trimethylene and pentamethylene glycols, i. e. glycols that show an odd number of methylene groups in their chain. The synthesis of the polyesters and their study has been described earlier [2, 4]. The obtained results are given in the table. Figs. 1 and 2 show the variation in the melting points of the polyesters as a function of the number of carbon atoms in the molecule of the starting dicarboxylic acid, from which it can be seen that the zigzag character of the dependence of the polyester melting points on the number of carbon atoms in the molecule of the starting acid, characteristic of polymethylene glycol polyesters with an even number of methylene groups in the polymethylene chain, is disrupted. This disruption begins with the polyesters of glutaric acid. Only for the polyesters of the first four members of the homologous dicarboxylic acid series (oxalic, malonic, succinic and glutaric) do we observe the characteristic zigzags. Beginning with polytrimethylene glutarate and polypentamethylene glutarate, an increase in the polyester melting points in measure with increase in the length of the methylene chain in the starting dicarboxylic acid proceeds as a smooth line. In the case of the trimethylene glycol polyesters the change proceeds almost linearly, while for the pentamethylene glycol polyesters it proceeds as a somewhat steeper curve. The difference in the melting points between polytrimethylene glutarate and polytrimethylene adipate is 1°, and between polypentamethylene glutarate and polypentamethylene adipate it is 14°. The character of the melting point changes for the polyesters of those dicarboxylic acids that contain only an even number of carbon atoms in their molecule, both for the polyesters of trimethylene glycol and for the polyesters of pentamethylene glycol, is similar to that of the earlier investigated polyesters of polymethylene glycols with an even number of methylene groups in the chain. The minimum melting points are found for the polyesters of adipic acid (polytrimethylene adipate and polypentamethylene adipate melt at 36°). Apparently, these polyesters appear as break points, where the softening influence of the simple ether linkage is shown in greatest measure, neutralizing, as it were, the influence shown by the polar carbonyl groups in increasing the melting point of the polymer. For the polyesters of trimethylene glycol the highest melting point is shown by the first member of the homologous series, namely polytrimethylene oxalate, the melting point of which is 66°. Polypentamethylene oxalate melts at 49°. A higher melting point for polytrimethylene oxalate than for polypentamethylene oxalate becomes comprehensible if we consider that the specific density of the polar carbonyl groups in the polytrimethylene oxalate molecule is greater than in the polypentamethylene oxalate molecule (in the first case there are 3 methylene groups for 2 carbonyl groups, and in the second case there are 5). The higher melting point shown by polytrimethylene succinate when compared to polypentamethylene succinate can also be explained by the same circumstance. The question as to the influence of various groups of atoms on the melting points of polyesters was examined by us in detail earlier [4, 5]. For the polyesters obtained from either trimethylene glycol or pentamethylene glycol and dicarboxylic acids with an odd number of carbon atoms in their molecule

TABLE

Polyesters	Temperature: melting	Temperature: flow	Temperature: of transition into the visco-liquid state	Solubility (in g/liter) in ethyl alcohol	Specific viscosity of a 0.5% polymer solution in benzene	Molecular weight
$-CO-CO-O(CH_2)_3O-$	66—68	—	—	7.5	0.22 *	4650
$-COCH_2COO(CH_2)_3O-$	—25; —21	—	—	5.1	0.023	900
$-CO(CH_2)_2COO(CH_2)_3O-$	43—45	—	—	4.2	0.048	1800
$-CO(CH_2)_3COO(CH_2)_3O-$	35—37	—	—	7.33	0.05	1850
$-CO(CH_2)_4COO(CH_2)_3O-$	36—37	41	39	20.5	0.03	1100
$-CO(CH_2)_4COO(CH_2)_3O-$	36—37	—	—	—	0.035	
$-CO(CH_2)_4COO(CH_2)_3O-$	36—37	—	—	7.25	0.089	3240
$-CO(CH_2)_5COO(CH_2)_3O-$	41—42	44	43	22.5	0.048	1720
$-CO(CH_2)_6COO(CH_2)_3O-$	44—45	—	—	—	0.085	2990
$-CO(CH_2)_7COO(CH_2)_3O-$	47—49	55	53	27.5	0.069	2240
$-CO(CH_2)_8COO(CH_2)_3O-$	49—51	56	54	24.8	0.062	2150
$-CO(CH_2)_{12}COO(CH_2)_3O-$	64—66	68	66	—	0.16	4400
$-CO-COO-(CH_2)_5O-$	49—54	—	—	4.1	0.147	5530
$-COCH_2COO(CH_2)_5O-$	—26 to —22	—	—	4.6	0.049	1690
$-CO(CH_2)_2COO(CH_2)_5O-$	32—35	—	—	5.3	0.101	3590
$-CO(CH_2)_3COO(CH_2)_5O-$	22—25	—	—	12.05	0.077	2740
$-CO(CH_2)_4COO(CH_2)_5O-$	37—40	—	—	15.8	0.053	1880
$-CO(CH_2)_4COO(CH_2)_5O-$	36—40	42.5	40	—	0.067	2380
$-CO(CH_2)_5COO(CH_2)_5O-$	39—43	—	—	9.4	0.056	1960
$-CO(CH_2)_5COO(CH_2)_5O-$	39—43	41.5	39	—	0.07	2450
$-CO(CH_2)_6COO(CH_2)_5O-$	43—46	—	—	—	0.045	1560
$-CO(CH_2)_7COO(CH_2)_5O-$	46—50	—	—	6.2	0.096	3290
$-CO(CH_2)_7COO(CH_2)_5O-$	46—50	49.5	47.5	—	0.09	3100
$-CO(CH_2)_8COO(CH_2)_5O-$	53—57	—	—	4.1	0.087	2920
$-CO(CH_2)_8COO(CH_2)_5O-$	53—57	55	54	—	0.088	2990
$-CO(CH_2)_{10}COO(CH_2)_5O-$	58—60	60	59	—	0.07	2380

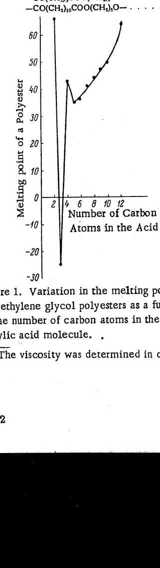

Figure 1. Variation in the melting points of trimethylene glycol polyesters as a function of the number of carbon atoms in the dicarboxylic acid molecule.

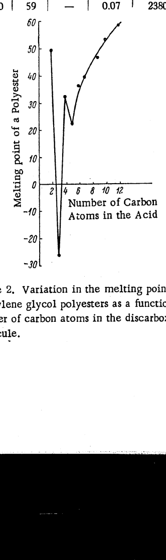

Figure 2. Variation in the melting points of pentamethylene glycol polyesters as a function of the number of carbon atoms in the discarboxylic acid molecule.

* The viscosity was determined in cresol.

the picture observed for variation in the melting points of the polymers as a function of the number of methylene groups in the dicarboxylic acid is the same as for the polyesters of other polymethylene glycols. Thus, with increase in methylene groups in the dicarboxylic acid the melting point of the polyester rises sharply between the polyesters of malonic and glutaric acid and then it shows a smoother rise for the polyesters of the subsequent dicarboxylic acids. For the polyesters of trimethylene glycol and pentamethylene glycol the character of the changes for the flow points and for the temperatures of transition into the visco-liquid state as a function of the number of carbon atoms in the dicarboxylic acid is similar to the character of the melting point changes. The flow points and temperatures of transition into the visco-liquid state show an increase for the polyesters with increase in the length of the methylene chain in the dicarboxylic acid, i. e. they increase from the polyesters of adipic acid to the polyesters of sebacic acid. For the investigated trimethylene glycol and pentamethylene glycol polyesters the temperature interval between the flow point and the temperature of transition into the visco-liquid state is small and constitutes a total of only 1-2°, which indicates the high degree of crystallinity of the given polymers. Determination of the alcohol solubility of the trimethylene glycol polyesters (Fig. 3) revealed that the variation in the alcohol solubility of the given polyesters as a function of the number of carbon atoms in the dicarboxylic acid molecule was different from that of the polyesters of polymethylene glycols, containing an even number of methylene groups in their molecule. The curve fails to be zigzag, and instead is a smooth line with a maximum corresponding to the polyester of azelaic acid. However, a comparison of solubilities in the polyester series, the same as for other polymers, should be approached with caution, for apparently the molecular weight of the polymer shows great influence on its ability to dissolve in various solvents. Thus, for example, polytrimethylene adipate, with a specific viscosity of 0.03 for its 0.5% solution in benzene, shows a solubility of 20.5 g/liter in ethyl alcohol, while polytrimethylene adipate, with a specific viscosity of 0.089, shows a total solubility of only 7.25 g/liter. Consequently, the decrease in the alcohol solubility of the given polymers is nearly proportional to the increase in their specific viscosities, i.e. in their molecular weights. Proceeding from this, the numerical data on the solubilities of our polymers in ethyl alcohol should be considered as being applicable only to the given sample with a definite specific viscosity. However, for the polyesters of trimethylene glycol and pentamethylene glycol we believe that our graph, showing the relationship between variation in the solubilities of polyesters and the number of carbon atoms in the starting dicarboxylic acid, despite the existing variations in the molecular weights of the investigated polymers, in general validly expresses the existing relationship. The polyesters derived from trimethylene glycol and succinic, glutaric and pimelic acids have approximately the same molecular weights, i. e. they all show comparable solubilities. The polyester of adipic acid shows somewhat higher solubility due to its lower molecular weight. Polyethylene adipate, with a specific viscosity of 0.05, will show a solubility in alcohol of approximately 12.5 g/liter. Evidently, for polytrimethylene azelate and polytrimethylene adipate the alcohol solubility will be somewhat lower due to the higher molecular weight of these polymers; however, the character of the curve for the variation in solubility as a function of the number of carbon atoms in the dicarboxylic acid will fail to change as a result of this, although the absolute solubility values will be different. The polyesters of pentamethylene glycol show much better solubility in benzene than they do in alcohol. Thus, most of the pentamethylene glycol polyesters, taken in amounts ranging from 0.8 to 1.6 g, are completely soluble in 5 ml of benzene.

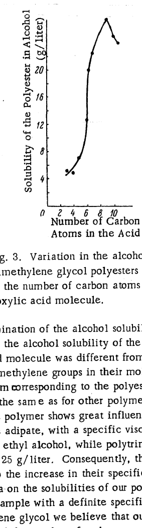

Fig. 3. Variation in the alcohol solubility of trimethylene glycol polyesters as a function of the number of carbon atoms in the dicarboxylic acid molecule.

SUMMARY

1. Polyesters of pentamethylene glycol and trimethylene glycol with dicarboxylic acids of general formula $HOOC(CH_2)_nCOOH$, with n ranging from 0 to 10, were prepared and studied.

2. The question as to the influence of the structure of the starting components on the melting points, flow points, temperatures of transition into the visco-liquid state, and solubilities of the obtained polyesters was examined.

3. Beginning with the polyesters of glutaric acid, it was shown that the presence of an odd number of methylene groups in the chain of the starting glycol leads to suppression of the evenness factor.

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SYNTHESIS OF ω, ω' - DIAMINO-p-XYLENE AND ITS DERIVATIVES

I. P. Losev, O. Ya. Fedotova and M. L. Kerber

ω, ω'- Diamino-p-xylene was first obtained in 1895 by Lustig [1] under the name of p-xylylenediamine, as its hydrochloride $C_6H_4(CH_2NH_2 \cdot HCl)_2 + 1.5\ H_2O$, by the condensation of xylene dibromide with potassium phthalimide. Lustig also prepared some derivatives of this amine (the chloroplatinate, picrate, tetraacetyl and dibenzoyl derivatives). F. Beilstein gives a melting point of 35° for the amine [2], not showing the author who determined this constant. Other data on the synthesis of the diamine is not encountered, although there is information [3] on its attempted use for the synthesis of polyamides. Proceeding from the presence of an amino group in the side chain, it can be assumed that its properties will be closer to those of the fatty rather than the aromatic amines, as is the case for benzylamine, in which connection the basic character of ω, ω'-diamino-p-xylene should be expressed even more clearly. In particular, the possibility of obtaining its salts with dicarboxylic acids seemed of interest, which is of very great importance for the synthesis of polyamides. The salts of ω, ω'-diamino-p-xylene with dicarboxylic acids (other than its salts with sebacic acid [4] and para-phenylenediacetic acid [5]) have not been described.

Considering the availability of ω, ω'-dichloro-p-xylene, otherwise known as p-xylylene dichloride, we attempted to obtain the diamine from it, identical with the p-xylylenediamine obtained by Lustig, through the hexamethylenetetramine complex. Here the reaction for the formation of ω, ω'-diamino-p-xylene should proceed by the following scheme:

$$C_6H_4(CH_2Cl)_2 + 2(CH_2)_6N_4 \longrightarrow C_6H_4(CH_2Cl)_2 \cdot (C_6H_{12}N_4)_2,$$
$$C_6H_4(CH_2Cl)_2 \cdot (C_6H_{12}N_4)_2 + 6HCl + 24C_2H_5OH \longrightarrow$$
$$\longrightarrow 12CH_2(OC_2H_5)_2 + C_6H_4(CH_2NH_2 \cdot HCl)_2 + 6NH_4Cl$$
$$C_6H_4(CH_2NH_2 \cdot HCl)_2 + 2NaOH \longrightarrow C_6H_4(CH_2NH_2)_2 + 2NaCl + 2H_2O.$$

Our experiments on the synthesis of ω, ω'-diamino-p-xylene from ω, ω'-dichloro-p-xylene by the Houben method [6], proposed by him for the conversion of benzyl chloride to benzylamine, showed that considerable modifications of this method have to be made, due to the specific properties shown by ω, ω'-diamino-p-xylene. The isolation of the diamine from the reaction mixture by distillation, as is the case for the synthesis of benzylamine, is not possible. An attempt to obtain the diamine by a modified method [7] failed to give a positive result. The reaction was appreciably hastened only in the first stage of obtaining the complex. The small amount of ω, ω'-diamino-p-xylene that was obtained proved to be highly contaminated with iodide salts. Its capacity for CO_2 sorption from the air determines the difficulty of isolating ω, ω'-diamino-p-xylene as the free base, which was not observed in Lustig's work, since he failed to isolate the diamine as the free base. On contact with the atmosphere the liquid diamine reacts with CO_2, being converted into an infusible and insoluble crystalline powder. The passage of CO_2 gas into an alcohol solution of ω, ω'-diamino-p-xylene also gives a crystalline precipitate of the carbonate. We failed to isolate the free diamine from its carbonate either with 25% ammonia or with alkali solutions. Treatment of the carbonate with hydrochloric acid gives the hydrochloride of the diamine. From our experimental results we developed a method for the synthesis of ω, ω'-diamino-p-xylene through the complex with urotropine (hexamethylenetetramine). To characterize the diamine

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we prepared ω, ω'-diamino-p-xylene, and also its salts with malonic, succinic, adipic and sebacic acids. Heating of the salts gave polyamides with a specific viscosity ranging from 0.19 to 0.27 for their 0.5% solutions in cresol, which corresponds to a molecular weight of 8000-10,000.

EXPERIMENTAL

Synthesis of ω, ω'-diamino-p-xylene. 6 g ω, ω'-dichloro-p-xylene with m. p. 100° (from alcohol) and 9 g urotropine were dissolved in 100 ml chloroform or in 200 ml methylene chloride. The main bulk of the complex compound separated out after standing for 24 hours at room temperature, the crystalline precipitate was filtered off, pressed out and dried in air. After 40 hours of standing, the yield was 95-96%. The obtained complex compound and the calculated (according to the reaction) quantity of hydrochloric acid and ethanol were boiled on a water bath with reflux condenser for 3 hours. The ethylal was then driven off at 70-80°. The operation was repeated two more times, heating the mixture with decreased ($^1/_2$ to $^1/_3$) quantities of hydrochloric acid and alcohol for 1 hour. The total quantity of the mixture of hydrochloric acid and ethanol exceeded the quantity calculated on the reaction by 1.7 times. The precipitate of hydrochloride was filtered off, washed free of acid with alcohol or acetone and dried at 60-70°. Upon treatment of the precipitate with 40% alkaline solution, the diamine separated out in the form of yellow-brown oily liquid. After vacuum-distillation in a stream of nitrogen or ammonia at 230° (10 mm), it had m. p. 37°. Yield 56%, calculated on ω, ω'-dichloro-p-xylene.

ω, ω'-Diamino-p-xylene was soluble in water, alcohols, difficultly soluble in ether, insoluble in acetone. Upon treatment with excess of acetic anhydride at room temperature, the diamine gave the diacetyl derivative with m. p. 225° (from alcohol – acicular crystals).

Found %: C 65.71; H 7.61; N 12.36. $C_{12}H_{16}O_2N_2$. Calculated %: C 65.42; H 7.32; N 12.72.

Mixing of 10% alcoholic solutions of ω, ω'-diamino-p-xylene and dicarboxylic acids (malonic, succinic, adipic and sebacic) brought down white crystalline precipitates of the neutral salts, the melting points of which are given in the table.

Acid	Melting point of salts	Melting point of polyamides
Malonic	181-182° (with decomp.)	108-110°
Succinic	228-230	189-192
Adipic	235-238 (with change of color)	280-285
Sebacic	215-218 (with change of color)	290-295

Salt of ω, ω'-diamino-p-xylene with malonic acid.

Found %: C 54.75; H 7.0; N 11.9. $C_{11}H_{16}N_2O_4$. Calculated %: C 55.0 ; H 6.66; N 11.66.

Salt of ω, ω'-diamino-p-xylene with succinic acid.

Found %: C 56.60; H 7.29; N 11.33. $C_{12}H_{18}N_2O_4$. Calculated %: C 56.69; H 7.09; N 11.03.

Salt of ω, ω'-diamino-p-xylene with adipic acid.

Found %: C 58.50; H 7.84; N 10.03. $C_{14}H_{22}N_2O_4$. Calculated %: C 59.57; H 7.8; N 9.93.

Salt of ω, ω'-diamino-p-xylene with sebacic acid.

Found %: C 63.4; H 8.60; N 7.91. $C_{18}H_{30}N_2O_4$. Calculated %: C 63.90; H 8.87; N 8.25.

Heating of the fused salts in cresol at 220-240° with subsequent evaporation of water and solvent in high vacuum (10^{-4} mm) yielded polyamides, a 0.5% solution of which in cresol had a specific viscosity of 0.19-0.27 and had a high surface tension and melted in the range 110-290° (see table).

SUMMARY

1. ω, ω'-Diamino-p-xylene was obtained from ω, ω' dichloro-p-xylene through the urotropine complex by a modification of Houben's method.

2. It was established that ω, ω'-diamino-p-xylene is capable of forming the carbonate when a CO_2 stream is passed into its alcohol solution, and is also capable of CO_2 sorption from the air. Under the influence of hydrochloric acid the carbonate is converted into the hydrochloride.

3. ω, ω'-Diacetamino-p-xylene and the salts of ω, ω'-diamino-p-xylene with malonic, succinic and adipic acids were obtained and described for the first time. The corresponding polyamides were obtained when the salts were heated.

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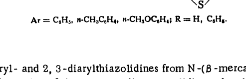
SYNTHESIS OF 3-ARYL- AND 2, 3-DIARYLTHIAZOLIDINES

Yu. K. Yuryev and L. S. German

Compounds of the thiazolidine series, devoid of functional groups, have shown comparatively little study and are described in the researches dealing with the preparation of thiazolidine itself and of 2-substituted thiazolidines. Thus, thiazolidine hydrochloride was obtained by the condensation of β-aminoethylmercaptan hydrochloride with formaldehyde [1]. The 2-substituted thiazolidines were obtained by the condensation of ethylenimine with certain carbonyl compounds in the presence of hydrogen sulfide [2]. The condensation of β-aminoethyl mercaptan hydrochloride with aldehydes and ketones, studied by S. V. Tsukerman, also led to obtaining 2-substituted thiazolidines [3].

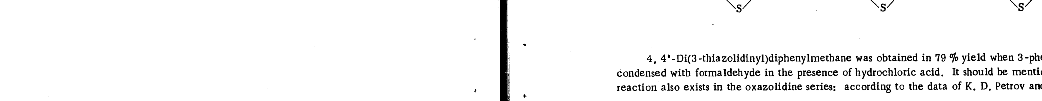
In studying the reaction of ethylene sulfide with aromatic amines we obtained a number of N-(β-mercaptoethyl) arylamines. In this paper we reacted some of them with formaldehyde and with benzaldehyde, and obtained respectively 3-aryl- and 2, 3-diarylthiazolidines:



$Ar = C_6H_5$, n-$CH_3C_6H_4$, n-$CH_3OC_6H_4$; $R = H$, C_6H_5.

The formation of 3-aryl- and 2, 3-diarylthiazolidines from N-(β-mercaptoethyl) arylamines proceeds in a manner similar to the formation of the corresponding oxazolidines when N-(β-hydroxyethyl)-arylamines are condensed with aldehydes [4].

The sole reaction products obtained in the condensation of N-(β-mercaptoethyl)-p-toluidine and N-(β-mercaptoethyl)-p-anisidine with formaldehyde were respectively 3-(p-tolyl) thiazolidine and 3-(p-anisyl) thiazolidine. When N-(β-mercaptoethyl)aniline, a compound with an aromatic ring devoid of para-substitution, was reacted with formaldehyde the 3-phenylthiazolidine that was formed here showed further condensation with the excess formaldehyde present, as a result of which 4, 4'-di (3-thiazolidinyl)-diphenylmethane was obtained as a reaction by-product:



4, 4'-Di(3-thiazolidinyl)diphenylmethane was obtained in 79 % yield when 3-phenylthiazolidine was condensed with formaldehyde in the presence of hydrochloric acid. It should be mentioned that a similar reaction also exists in the oxazolidine series: according to the data of K. D. Petrov and O. K. Gosteva the

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reaction of 3-phenyloxazolidine with formaldehyde leads to the formation of 4, 4'-di (3-oxazolidinyl) diphenylmethane [5].

EXPERIMENTAL

3-Phenylthiazolidine. a) A mixture of 7.6 g (0.05 mole) N-(β-mercaptoethyl)-aniline and 25 ml 30% formalin (0.25 mole) were shaken for 1.5 hours on a rocker. The resulting crystalline precipitate was separated off on a funnel, cooled with ice, and then it was washed with ice water and dried in a vacuum-desiccator. Yield 8.2 g substance which melted at 25-96° and which upon fractional crystallization from 80% alcohol, yielded 4.2 g (51%) substance with m. p. 31-32° and 0.8 g (9%) substance with m. p. 134-137° (with decomp.).

The crystals with m. p. 31-32° gave a positive reaction for nitrogen and sulfur and a negative reaction for the mercapto group, were readily soluble in alcohol, ether, acids, insoluble in water, and were 3-phenylthiazolidine.

Found %: N 8.87, 8.83; S 19.36, 19.38. $C_9H_{11}NS$. Calculated %: N 8.49, S 19.45.

After 2 hours boiling with hydrochloric acid, 3-phenylthiazolidine gave no positive reaction for mercapto group and resinified upon heating with concentrated caustic soda solution*.

The crystals with m. p. 134-137° (with decomp.) also gave a positive reaction for nitrogen and sulfur, negative for mercapto group, were readily soluble in alcohol and in ether, insoluble in water and were 4, 4'-di'-(3-thiazolidyl)-diphenylmethane.

Found %: N 8.45, 8.37; S 18.59, 18.65. $C_{19}H_{22}N_2S_2$. Calculated %: N 8.17, S 18.72.

b) A mixture of 8 g (0.052 mole) N-(β-mercaptoethyl)-aniline, 25 ml 30% formalin (0.25 mole) and 0.8 g (0.01 mole) sodium bicarbonate was shaken on a rocker until there was no further formation of crystalline precipitate which was then further treated as described above. After recrystallization from 80% alcohol, the substance had m. p. 31-31.5° and was 3-phenylthiazolidine. Yield 8.5 g (98%). A melting test mixture with 3-phenylthiazolidine, obtained in the preceding experiment, gave no depression; m. p. 31-32°.

4, 4'-Di-(3-thiazolidyl)-diphenylmethane. 20 ml 30% formalin (0.2 mole), and then 1.5 ml hydrochloric acid (d 1.19) were added with vigorous stirring in the course of thirty minutes to a solution of 5 g (0.03 mole) 3-phenylthiazolidine in 50 ml alcohol contained in a 3-necked flask (100 ml) fitted with stirrer, reflux condenser and dropping funnel and the reaction mixture was then heated for 4 hours on a boiling water bath, and after only 20 minutes, a white precipitate began to separate out. After cooling and neutralization with sodium bicarbonate, the precipitate was separated, washed with water and dried in a vacuum-desiccator. After recrystallization from alcohol, the substance had m. p. 133-136° (with decomp.) and was 4, 4'-di-(3-thiazolidyl)-diphenylmethane. Yield 4.1 g (79%).

Found %: C 66.58, 66.55; H 6.41, 6.44; N 8.21, 8.30; S 18.59, 18.64. $C_{19}H_{22}N_2S_2$. Calculated %: C 66.63; H 6.47; N 8.17; S 18.72.

3-(p-Tolyl)-thiazolidine. A mixture of 4.2 g (0.025 mole) N-(β-mercaptoethyl)-p-toluidine and 20 ml 30% formalin (0.2 mole) was vigorously shaken for 15 minutes. The crystals which formed were

* In 1888 Forster ascribed the structure of 3-phenylthiazolidine to the reduction product of 3-phenylthiazolidone but gave no constants for the compound obtained [6].

separated and recrystallized from 80% alcohol. Yield 4.3 g (97%) substance which was 3-(p-tolyl)-thiazolidine; m. p. 79-80°.

Found %: N 8.07, 8.02; S 17.79, 17.83. $C_{10}H_{13}NS$. Calculated %: N 7.81; S 17.88.

The product was readily soluble in alcohol, ether, acids; insoluble in water; resistant to acid and alkaline hydrolysis in the course of 2 hours.

3-(p-Anisyl)-thiazolidine. A mixture of 4 g (0.022 mole) N-(β-mercaptoethyl)-p-anisidine and 20 ml 30% formalin (0.2 mole) was vigorously shaken for 15 minutes. After suitable treatment, the crystalline precipitate yielded 4.1 g (95%) substance which was 3-(p-anisyl)-thiazolidine; m. p. 84-85° (from 80% alcohol).

Found %: N 7.38, 7.47; S 16.33, 16.35. $C_{10}H_{13}ONS$. Calculated %: N 7.17; S 16.42.

The product was readily soluble in alcohol, ether, acids; insoluble in water; resisted acid and alkaline hydrolysis in the course of 2 hours.

2, 3-Diphenylthiazolidine. A mixture of 6 g (0.039 mole) N-(β-mercaptoethyl)-aniline in 15 ml alcohol and 26.5 g (0.25 mole) benzaldehyde was set aside for 48 hours until it gave no further reaction for the mercapto group. The reaction mixture was diluted with 15 ml water and cooled with and ice-salt mixture. The crystals which came down were separated, washed with cold alcohol and then with water. Yield 6.4 g (69%) substance which was 2, 3-diphenylthiazolidine; m. p. 86°.

Found %: N 6.00, 5.97; S 13.21, 13.22. $C_{15}H_{15}NS$. Calculated %: N 5.80; S 13.29.

The product was readily soluble in ether, acids; difficultly soluble in alcohol; insoluble in water. It was hydrolyzed with concentrated hydrochloric acid upon 30 minutes of heating (positive reaction of hydrolyzate for mercapto group).

2-Phenyl-3-(p-tolyl)-thiazolidine. From 4.3 g (0.026 mole) N-(β-mercaptoethyl)-p-toluidine in 15 ml alcohol and 21.2 g (0.2 mole) benzaldehyde, after the mixture had stood 48 hours, we obtained 5.1 g (77%) 2-phenyl-3-(p-tolyl)-thiazolidine; m. p. 86°. *

Found %: N 5.80, 5.68; S 12.48, 12.53. $C_{16}H_{17}NS$. Calculated %: N 5.48; S 12.56.

The product was readily soluble in ether, acids; difficultly – in alcohol; insoluble in water. It was hydrolyzed with concentrated hydrochloric acid upon heating for thirty minutes.

2-Phenyl-3-(p-anisyl)-thiazolidine. From 5 g (0.027 mole) N-(β-mercaptoethyl)-p-anisidine in 15 ml alcohol and 21.2 g (0.2 mole) benzaldehyde, after the mixture had stood 48 hours, we obtained 5.6 g (80%) 2-phenyl-3-(p-anisyl)-thiazolidine; m. p. 87°.

Found %: N 5.48, 5.34; S 11.77, 11.78. $C_{16}H_{17}ONS$. Calculated %: N 5.16; S 11.82.

The product was readily soluble in ether, acids; difficultly soluble in alcohol; insoluble in water. It was hydrolyzed upon heating for thirty minutes with concentrated hydrochloric acid.

* A melting test mixture with 2, 3-diphenylthiazolidine gave a melting point depression.

SUMMARY

1. The condensation of N-(β-mercaptoethyl)arylamines with formaldehyde and with benzaldehyde gave the previously unknown 3-phenyl-, 3-(p-tolyl)-, 3-(p-anisyl)-, 2, 3-diphenyl-, 2-phenyl-3-(p-tolyl)- and 2-phenyl-3-(p-anisyl)thiazolidine.

2. The condensation of 3-phenylthiazolidine with formaldehyde gave the previously unknown 4, 4'-di (3-thiazolidinyl) diphenylmethane.

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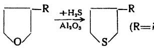
CATALYTIC TRANSFORMATIONS OF HETEROCYCLIC COMPOUNDS

XLVIII. PREPARATION OF 3-ISOAMYL-, 3-HEXYL- AND 3-p-TOLYLTETRAHYDROTHIOPHENES FROM THE CORRESPONDING FURANIDINES

Yu. K. Yuryev, E. M. Lukina, Yu. M. Polikarpov and V. P. Volkov

In one of our previous papers we had shown that the reaction of 3-furanidone (3-tetrahydrofuranone) with organomagnesium compounds can serve as a general method for the synthesis of 3-alkyl- and 3-arylfuranidines [1]. When we reacted the thus obtained 3-n-amylfuranidine and 3-phenylfuranidine with hydrogen sulfide in the presence of aluminum oxide at 350° we effected their respective conversion into 3-n-amyl-tetrahydrothiophene (64% yield) and 3-phenyltetrahydrothiophene (58% yield) [2]. In the last case, in contrast to the earlier described similar transformations of 3-alkylfuranidines [3], appreciable amounts of 2-phenyl-2-butene were obtained as a reaction by-product, which was due to the influence of the phenyl radical, attached to the β-carbon atom of the furanidine ring.

In the present study we used 3-furanidone in the organomagnesium synthesis of 3-isoamyl-, 3-n-hexyl- and 3-p-tolyl- furanidine.* When these compounds were reacted with hydrogen sulfide, under conditions used for the catalytic transformation of oxygen-containing heterocycles into cycles with other heteroatoms, we obtained 3-isoamyl-, 3-n-hexyl- and 3-p-tolyltetrahydrothiophene, respectively.



($R = iso\text{-}C_5H_{11}$, $n\text{-}C_6H_{13}$, $p\text{-}CH_3C_6H_4$).

A mixture of isomeric 2-p-tolylbutenes appeared as the by-product in the catalytic transformation of 3-p-tolylfuranidine. As in the case for the transformation of 3-phenylfuranidine into 3-phenyltetrahydrothiophene [2], the formation of these secondary reaction products is associated with the partial simultaneous cleavage of water and hydrogen sulfide from the intermediately arising diprimary 1, 4-mercaptohydroxy compound (1-hydroxy-2-p-tolyl-4-butanethiol), with subsequent hydrogen addition to the resulting 2-p-tolyl-1, 3-butadiene at the 1, 2-and the 1, 4-positions:

* It should be emphasized that the 3-hydroxy-3-alkylfuranidines formed in the first stage of the synthesis are dehydrated with greater difficulty than are the 3-hydroxy-3-arylfuranidines, in which connection the dehydration proceeds with better yields under the influence of p-toluenesulfonic acid than under the influence of iodine.

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EXPERIMENTAL

I. Synthesis of 3-hydroxy-3-alkyl- and 3-hydroxy-3-arylfuranidines was by the method described in the previous paper [1].

3-Hydroxy-3-isoamylfuranidine. From 7.8 g magnesium, 49.1 g isoamyl bromide and 28 g 3-furanidone in 300 ml ether we obtained 23.2 g (46.0 %) 3-hydroxy-3-isoamylfuranidine. Colorless liquid; readily soluble in alcohol, ether, sparingly soluble in water.

B. p. 86-87° (3 mm), 105-105.5° (10 mm), n_D^{20} 1.4549, d_4^{20} 0.9626, MR_D 44.60, Calc. 44.73. Found %: C 68.12; H 11.38. $C_9H_{18}O_2$. Calculated %: C 68.31; H 11.47.

3-Hydroxy-3-n-hexylfuranidine. From 7.05 g magnesium, 48 g n-hexyl bromide and 25 g 3-furanidone in 300 ml ether we obtained 24.8 g (49.5%) 3-hydroxy-3-n-hexylfuranidine.

B. p. 102-103° (3 mm), 99-99.5° (2 mm), n_D^{20} 1.4570, d_4^{20} 0.9556, MR_D 49.10, Calc. 49.35. Found %: C 69.55, 69.69; H 11.75, 11.86. $C_{10}H_{20}O_2$. Calculated %: C 69.72; H 11.70.

3-Hydroxy-3-p-tolylfuranidine. From 8.1 g magnesium, 56.4 g p-bromotoluene and 28.4 g 3-furanidone in 300 ml ether we obtained 29.7 (50%) 3-hydroxy-3-p-tolylfuranidine.

B. p. 123-123.5° (3 mm), n_D^{20} 1.5492, d_4^{20} 1.1230, MR_D 50.51. $C_{11}H_{14}O_2F_3$. Calc. 50.36. Found %: C 73.55, 73.62; H 8.14, 8.04. $C_{11}H_{14}O_2$. Calculated %: C 74.07; H 7.91.

II. Dehydration of 3-hydroxy-3-alkyl- and 3-hydroxy-3-arylfuranidines

3-Isoamyldihydrofuran. 23 g 3-hydroxy-3-isoamylfuranidine was dehydrated with 0.05 g p-toluenesulfonic acid upon slow distillation from a flask with a small fractional column. Distillation of the dried distillate yielded 7 g product of dehydration and 13.2 unchanged 3-hydroxy-3-isoamylfuranidine, which was again dehydrated in the above manner. Total yield 14.5 g (71 %) of 3-isoamyldihydrofuran. Dehydration with iodine did not yield above 60%.

B. p. 61.5-62.5° (10 mm), n_D^{20} 1.4522, d_4^{20} 0.8911, MR_D 42.21. $C_9H_{16}OF$. Calc. 42.74.

3-n-Hexyldihydrofuran. 24 g 3-hydroxy-3-n-hexylfuranidine and 0.1 g p-toluenesulfonic acid were heated in a flask fitted with fractional column. Slow distillation of the dehydration product followed by a repeated distillation yielded 16 g (79%) 3-n-hexyldihydrofuran.

B. p. 86-87° (10 mm), n_D^{20} 1.4545, d_4^{20} 0.8753, MR_D 47.71. $C_{10}H_{18}OF$. Calc. 47.36.

3-p-Tolyldihydrofuran. 26.5 g 3-hydroxy-3-p-tolylfuranidine and 0.25 g iodine were heated 1.5 hours on an oil bath at 210-220°. The reaction mixture was dissolved in ether, the ethereal solution was washed with 10 ml 10% soda solution, water and dried. After the ether was driven off, the residue was vacuum-distilled. Yield 21.3 g (89%) 3-p-tolyldihydrofuran in the form of colorless flaky crystals, deliquescent upon standing in air.

B. p. 102-105° (3 mm), m. p. (from anhydrous alcohol) 65-66°.

III. Catalytic hydrogenation of 3-alkyl- and 3-aryldihydrofurans was carried out in anhydrous alcohol in the presence of platinum oxide [4] in the cold with shaking.

3-Isoamylfuranidine. 14 g 3-isoamyldihydrofuran was hydrogenated in 30 ml anhydrous alcohol. 2020 ml (NTP) hydrogen was absorbed (calculated 2240 ml). The hydrogenation product was treated upon cooling with a solution of bromine in chloroform until the appearance of a persistant yellow coloration and set aside overnight. After being driven off from the bromides and vacuum-distillation over sodium we obtained 9.1 g (65%) 3-isoamylfuranidine.

B. p. 74.5-75° (20 mm), n_D^{20} 1.4350, d_4^{20} 0.8609. MR_D 43.11, Calc. 43.20.

Found %: C 75.56, 75.67; H 12.69, 12.54. $C_9H_{18}O$. Calculated %: C 75.92; H 12.74.

3-n-Hexylfuranidine. 15.8 g 3-n-hexyldihydrofuran was hydrogenated in 40 ml anhydrous alcohol. 2260 ml (NTP) hydrogen was absorbed (calculated 2300 ml). After suitable treatment and distillation of the hydrogenation product over sodium we obtained 10.7 g (68%) 3-n-hexylfuranidine.

B. p. 83.5-84.5° (10 mm), n_D^{20} 1.4428, d_4^{20} 0.8647, MR_D 47.89, Calc. 47.82.

Found %: C 76.33, 76.50; H 12.59, 12.67. $C_{10}H_{20}O$. Calculated %: C 76.79; H 12.88.

3-p-Tolylfuranidine. 19.2 g 3-p-tolyldihydrofuran was hydrogenated in 50 ml anhydrous alcohol. 2820 ml (NTP) hydrogen was absorbed (calculated 2700 ml). After suitable treatment of the hydrogenation product and distillation over sodium, we obtained 13.1 g (67.5%) 3-p-tolylfuranidine.

B. p. 95-95.5° (4 mm), n_D^{20} 1.5312, d_4^{20} 1.0156, MR_D 49.43. $C_{11}H_{14}OF_3$. Calc. 48.84.

Found %: C 81.26, 81.11; H 8.82, 8.83. $C_{11}H_{14}O$. Calculated %: C 81.44; H 8.70.

IV. Conversion of 3-alkyl- and 3-arylfuranidines to corresponding 3-alkyl- and 3-aryltetrahydrothiophenes was accomplished as described in the previous paper [2], by the action of hydrogen sulfide in the presence of aluminum oxide at 350°.

3-Isoamyltetrahydrothiophene. From 12.1 g 3-isoamylfuranidine we obtained 8.1 g (60%) 3-isoamyltetrahydrothiophene.

B. p. 87-88° (10 mm), n_D^{20} 1.4868, d_4^{20} 0.9196, MR_D 49.49, Calc. 49.63.

Found %: S 20.46. $C_9H_{18}S$. Calculated %: S 20.26. M. p. of compound with $HgCl_2$ (from alcohol) 104.5-105.5°.

Found %: Hg 46.80, 46.59. $C_9H_{18}SCl_2Hg$. Calculated %: Hg 46.68.

3-n-Hexyltetrahydrothiophene. From 14.8 g 3-n-hexylfuranidine we obtained 9.6 g (57%) 3-n-hexyltetrahydrothiophene.

B. p. 121-122° (16 mm), n_D^{20} 1.4870, d_4^{20} 0.9170, MR_D 54.05, Calc. 54.25.

Found %: S 18.58. $C_{10}H_{20}S$. Calculated %: S 18.61. M. p. of compound with $HgCl_2$ (from alcohol) 98-99°.

Found %: Hg 45.22, 45.29. $C_{10}H_{20}SCl_2Hg$. Calculated %: Hg 45.20.

3-p-Tolyltetrahydrothiophene. From 12.0 g 3-p-tolylfuranidine we obtained 6.7 g (51%) 3-p-tolyltetrahydrothiophene.

B. p. 127.5-128.5° (4 mm), n_D^{20} 1.5847, d_4^{20} 1.0645, MR_D 55.98. $C_{11}H_{14}SF_3$. Calc. 55.27.

Found %: S 17.84. $C_{11}H_{14}S$. Calculated %: S 17.99. M. p. of compound with $HgCl_2$ (from alcohol) 128.5-129°.

Found %: Hg 44.65, 44.70. $C_{11}H_{14}SCl_2Hg$. Calculated %: Hg 44.59.

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Distillation of the conversion product yielded 2.2 g of lower-boiling fraction which decolorized bromine water and potassium permanganate solution and contained no sulfur. A repeated distillation of this fraction yielded:

a) 1.4 g substance: b. p. 80-84° (12 mm), n_D^{20} 1.5288, d_4^{20} 0.8938, MR_D 50.46. $C_{11}H_{14}F_4$. Calc. 48.93.

Found %: C 90.04, 89.89; H 9.73, 9.84. $C_{11}H_{14}$. Calculated %: C 90.35; H 9.65.

b) 0.5 g substance: b. p. 93-98° (12 mm), n_D^{20} 1.5386, d_4^{20} 0.8994, MR_D 50.92. $C_{11}H_{14}F_4$. Calc. 48.93.

Found %: C 89.93, 89.86; H 9.31, 9.32. $C_{11}H_{14}$. Calculated %: C 90.35; H 9.65.

The analytical data, constants and properties of the isolated hydrocarbons indicate that the side product of the conversion of 3-p-tolylfuranidine to 3-p-tolyltetrahydrothiophene is a mixture of 2-p-tolyl-1-butene (fraction with b. p. 80-84° at 12 mm) and 2-p-tolyl-2-butene (fraction with b. p. 93-98° at 12 mm) with 2-p-tolyl-1-butene predominating.

Literature data for 2-p-tolyl-1-butene give: b. p. 206-209°, n_D^{20} 1.52735, d_4^{20} 0.8926 [5].

Literature data for 2-p-tolyl-2-butene give: b. p. 93.5-94° (10 mm) [6].

2-p-Tolyl-3-butene is not described in the literature; its presence in the hydrocarbon mixture is doubtful since in contact with aluminum oxide at high temperatures it undergoes isomerization with transposition of the double bond to the aromatic ring [7], i.e., with formation of a hydrocarbon of the styrene type – 2-p-tolyl-2-butene.

SUMMARY

1. The previously unknown 3-isoamylfuranidine, 3-n-hexyl-furanidine and 3-p-tolylfuranidine were obtained by the general method developed by us, namely the reaction of 3-furanidone with organomagnesium compounds, followed by dehydration of the thus obtained tertiary alcohols, and finally catalytic hydrogenation of the dehydration products.

2. 3-Isoamyltetrahydrothiophene, 3-n-hexyltetrahydrothiophene and 3-p-tolyltetrahydrothiophene were obtained by us for the first time by the catalytic transformation of 3-isoamyl-, 3-n-hexyl- and 3-p-tolylfuranidine, respectively.

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SYNTHESES WITH ACRYLONITRILE

XXV. CYANOETHYLATION OF INDOLE

A. P. Terentyev, A. N. Kost and V. A. Smit

β-Indolyl-β-propionic acid has been described in the literature as a root-formation stimulant [1]. The methods for its preparation through phenylhydrazones are very complicated [2].

Proceeding from indole, this acid can be obtained by the action of either diazosuccinic ester [3] or of propiolactone [4]. According to patent data, β-indolyl-β-propionitrile can be obtained in good yield by reacting indole with acrylonitrile [5, 6], which is then easily saponified to the corresponding acid [7]. In the patent of Reppe and Ufer [5] it is indicated that the reaction of indole with acrylonitrile under the influence of either acidic or alkaline agents yields β-indolyl-β-propionitrile. The addition of copper salts fails to influence the direction of the reaction in alkaline medium, but in acetic acid medium the β-isomer is formed exclusively. The reaction proceeds in similar manner with α-methylindole, but α-phenylindole, even without the addition of copper salts, shows cyanoethylation in the β-position. In addition, data show[6] that in alkaline medium also the addition of copper salts partially facilitates β-isomer formation.

Reppe's data are only partially supported by our experiments. In acid media (without the addition of copper salts) the N-cyanoethylation products of indole were not found. Reppe indicates that α-methylindole in the presence of monochloroacetic acid, without the addition of copper salts, is cyanoethylated on the nitrogen and when saponified yields N-(α-methylindolyl)-β-propionic acid with m. p. 135°. Actually, this substance proved to be the β-isomer, which we showed by cyanoethylation of the β-isomer [7] and conversion of the N, β-(α-methylindolylidene)-di-β-propionic acid into β-(α-methylindolyl)-β-propionic acid. It is possible to assume that the error made by Reppe is associated with the fact that copper parts were present in his apparatus. In ampoule without copper traces the reaction fails to proceed; with the introduction of copper foil the β-isomer is formed.

The cyanoethylation of indole under the Reppe conditions (16 hours, 130-140°) gave us β-indolyl-β-propionitrile in up to 50% yield. If the reaction is run in benzene medium, introducing 4 moles of acrylonitrile for 1 mole of indole, the yield reaches 81%. It is interesting to mention that the yield depends in considerable measure on the indole purity and the apparatus material (the yields are lower in glass ampoules than in an autoclave). Without boric acid (i.e., with copper acetate) the yield drops to 44%, while without acetic acid the β-indolyl-β-propionitrile is obtained only in small amounts. Here it is possible to assume that acetic acid increases the solubility of copper borate and in that way hastens the process. Actually, if copper acetylacetonate is introduced instead of copper borate, or even better, either copper salicylalimine or copper salicylalanyl, then even without the addition of either acetic or boric acid the yields obtained are as high as 60%. The addition of boric acid in this case lowers the yield; if acetic acid is added the yield reaches 80%.

To elucidate the reaction mechanism it could be postulated that the first-formed N-indolyl-β-propionitrile (under the influence of temperature and catalysts) suffers rearrangement in the β-position, either directly or through the intermediate formation of the N, β-dinitrile. However, under these conditions the N-indolyl-β-propionitrile fails to show conversion into the β-isomer and is not cyanoethylated in the β-position. N-Methylindole also fails to react with acrylonitrile under these conditions.

The assumption of previous indole acylation on the nitrogen (which determines the change in orientation) is also removed by the cyanoethylation experiments without the addition of acids (with copper salicylalimines).

As a result, the cyanoethylation evidently proceeds directly at the β-position (possibly, with preliminary isomerization into the indolenine form).

EXPERIMENTAL

Perfumery indole, steam-distilled and then vacuum-distilled, was used; acrylonitrile – stabilized with hydroquinone.

β-Indolyl-β-propionitrile. A mixture of 11.7 g indole, 21.2 g acrylonitrile, 10 ml benzene, 0.3 g glacial acetic acid, 0.2 g copper acetate and 0.07 g boric acid was heated in a steel autoclave (90 ml) for 6 hours at an oil bath temperature of 180-190°. After cooling, the autoclave was opened, the red solution with a small quantity of brown precipitate was transferred to a Claisen flask and the autoclave was carefully washed with benzene. After driving off the solvent, the residue was vacuum-distilled in a stream of nitrogen. Yield 2.5 g of fraction which boiled up to 190° at 3 mm (mostly indole) and 13.8 g (81%) β-indolyl-β-propionitrile with b. p. 190-210° at 3 mm and m. p. 62°. After crystallization from benzene it had m. p. 67-68°. The literature data give: 63-64° [5], 67-68° [8]. When the temperature was raised to 210-220°, the yield was reduced 10-12%. When 2 moles acrylonitrile was used, the yield was 73%. In an ampoule the yield did not exceed 60%. Increase of the amount of acetic acid decreased the yield.

A mixture of 17 g β-indolyl-β-propionitrile with 80 ml 25% caustic soda solution was boiled for 2 hours. Upon cooling, crystals of the potassium salt of β-indolyl-β-propionic acid came down. The salt was dissolved upon adding the required quantity of water and after filtration of the solution, β-indolyl-β-propionic acid was brought down in the form of white crystals by acidification of the solution with hydrochloric acid (1 : 3). After drying in a desiccator over calcium chloride, it weighed 17 g (90%), m. p. 133°. Literature data give: m. p. 132° [5], 133-134° [8].

Cyanoethylation of indole in the presence of organic copper complexes. A mixture of 11.7 g indole, 21.2 g acrylonitrile, 10 ml benzene, 0.3 g copper salicylalanyl and 0.3 g acetic acid was heated for 6 hours in an autoclave (90 ml) at 180-190°. After the usual treatment, we obtained 2.4 g indole and 13.6 g (80%) β-indolyl-β-propionitrile.

Addition of cuprous chloride, copper foil or cuprous oxide only slightly catalyzed the reaction (yields of 10-17 %). Nickel formate, nickel dimethylglyoximate and cobalt salicylalanyl did not catalyze the reaction. Without acid additions with copper salicylalanyl the yield was 52%, with copper salicylalimine – 56%, with copper acetylacetonate – 38%. Additions of boric acid in the last case reducted the yield to 15%.

β-(α-Methylindolyl)-β-propionitrile. A mixture of 9.1 g α-methylindole, 7.4 g acrylonitrile, 10 ml benzene, 0.2 g glacial acetic acid, 0.05 g boric acid and 0.15 g copper acetate was heated in a steel autoclave (90 ml) for 6 hours at oil bath temperature of 180-190°. The treatment and separation of the reaction product were the same as in the preceding experiment. Yield: 0.8 g α-methylindole, b. p. 120-135° at 3 mm and 10.3 g (81%) β-(α-methylindolyl)-β-propionitrile with b. p. 203-209° at 2 mm and m. p. 72°. After 3 crystallizations from aqueous methanol, it had m. p. 79.5°.

Found %: C 78.36, 78.75; H 6.46, 6.64. $C_{12}H_{12}N_2$. Calculated %: C 78.26; H 6.52.

A mixture of 3.7 g β-(α-methylindolyl)-β-propionitrile and 25 ml 10% caustic soda solution was boiled for 3 hours. After filtration, cooling and acidification, we obtained 3 g β-(α-methylindolyl)-β-propionic acid. After recrystallization from water it had m. p. 138° (it was unchanged by a repeated recrystallization). Literature data give: m. p. 138° [9].

Cleavage of N, β-(α- methylindolidene)di-β-propionic acid. Steam, superheated to 300°, was passed in the course of 1 hour into a solution of 2.8 g N, β-(α-methylindolidene)-di-β-propionic acid [7] in 10 ml 50% caustic soda solution. The residue in the distilling flask was dissolved in water, filtered and acidified with 10% hydrochloric acid. The β-(α-methylindolyl)-β-propionic acid which came down was separated and dried in a desiccator over calcium chloride. Yield 1.6 g (80%) acid with m. p. 138°. The literature data give: m. p. 138° [9]. It gave no melting point depression with the acid prepared from β-(α-methylindolyl)-β-propionitrile [7].

SUMMARY

The conditions for the cyanoethylation of indole and of α-methylindole in the β-position were investigated. It was found that copper borate, proposed by Reppe as a catalyst, can be replaced by organic copper complexes. Reaction in this case then proceeds even in the absence of acids.

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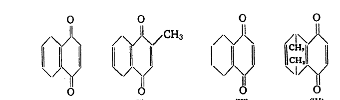
QUINONES

VII. SYNTHESIS OF SOME QUINONES OF THE DIHYDRO- AND TETRAHYDRONAPHTHALENE SERIES BY OXIDATION OF THE CORRESPONDING HYDROQUINONES WITH POTASSIUM BROMATE

A. N. Grinev, A. B. Terentyev and A. P. Terentyev

In our previous paper [1] we communicated that potassium bromate in acid medium is a very convenient reagent for the oxidation of halo-substituted hydroquinones to the corresponding quinones. In the present study we obtained some quite difficultly available quinones of the dihydro- and tetrahydronaphthalene series in nearly quantitative yields by this method. According to the data of other authors [2, 3], these quinones are obtained in considerably lower yields by the oxidation of hydroquinones with ferric chloride.

The oxidation of hydroquinones with potassium bromate gave us: 5, 8-dihydro-1, 4-naphthoquinone (I), 2-methyl-5, 8-dihydro-1, 4-naphthoquinone (II), 5, 6, 7, 8-tetrahydro-1, 4-naphthoquinone (III) and 5, 8-endo-ethylene-5, 8-dihydro-1, 4-naphthoquinone (IV):



(I) (II) (III) (IV)

The oxidation of hydroquinones to quinones was run in aqueous dioxane solutions, since difficultly water-soluble quinhydrones are formed in the reaction process. Reaction is both rapid (3-5 minutes) and smooth. The quinones immediately separate from the reaction mixture as well-formed crystals with sharp and constant melting points, and do not require purification.

EXPERIMENTAL

5, 8-Dihydro-1, 4-naphthoquinone (I). 4 g 5, 8-dihydro-1, 4-naphthohydroquinone (m. p. 212°), prepared by the Diels-Alder method [2], was dissolved in 40 ml dioxane with heating. 2 g potassium bromate in 20 ml hot water and 2 ml 1 N sulfuric acid (in place of dioxane acetic acid may be used without addition of sulfuric acid) were added to the above solution. The reaction mixture was heated to 60° while stirring; at first a dark red coloration appeared which turned light yellow. Upon cooling, crystals of quinone came down and were separated. A further quantity of quinone precipitated from the mother liquor when it was diluted with water. Since the substance quite readily altered in a moist state and in light, it was necessary to dry it in the dark in a vacuum-desiccator over phosphoric anhydride. Yield 3.8 g quinone; m. p. 109°, which corresponded to the literature data [2]. The quinone was readily soluble in ether, benzene, alcohol and in dioxane. In ethereal and benzene solutions the quinone readily darkened; it stored well upon cooling with ice under water.

2-Methyl-5, 8-dihydro-1, 4-naphthoquinone (II) was prepared by addition of divinyl to toluquinone and isomerization of the initially formed adduct [4]. The prepared hydroquinone (m. p. 168°) was treated as before. For the experiment we took methyldihydronaphthohydroquinone 1 g, potassium bromate 0.5 g, dioxane 10 ml, water 5 ml, 1 N sulfuric acid 1 ml. Yield 0.9 g quinone – light-yellow crystals with m. p. 86° (literature data give m. p. 85-86°), darkened upon storage.

5, 6, 7, 8-Tetrahydro-1, 4-naphthoquinone (III). The initial 5, 6, 7, 8-tetrahydro-1, 4-naphthohydroquinone (m. p. 185°) was prepared by the Diels-Alder method [2]. Taken for experiment: 1 g hydroquinone, 0.5 g potassium bromate, 9 ml dioxane, 5 ml water, 0.7 ml 1 N sulfuric acid. The reaction and isolation of the product were performed as before. Yield 0.9 g quinone with m. p. 54° (literature data: m. p. 55.5° [2]).

5, 8-Endoethylene-5, 8-dihydro-1, 4-naphthoquinone (IV) was prepared by isomerization of the adduct formed by addition of cyclohexadiene to p-benzoquinone [2]. M. p. of hydroquinone 178°. For the experiment we took 1 g hydroquinone, 0.5 g potassium bromate, 0.8 ml 1 N sulfuric acid, 10 ml dioxane, 6 ml water. Yield 0.87 g quinone. M. p. 99° (literature data: m. p. 99°).

SUMMARY

Oxidation of hydroquinones in the dihydro- and tetrahydronaphthalene series with potassium bromate gave: 5, 8-dihydro-1, 4-naphthoquinone, 2-methyl-5, 8-dihydro-1, 4-naphthoquinone, 5, 6, 7, 8-tetrahydro-1, 4-naphthoquinone and 5, 8-endoethylene-5, 8-dihydro-1, 4-naphthoquinone.

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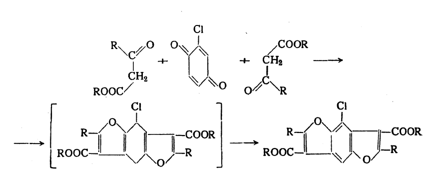
QUINONES

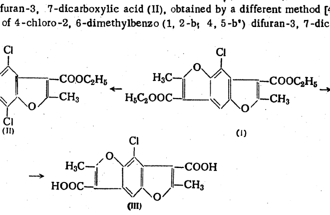
VIII. CONDENSATION OF CHLORO- AND 2, 3-DICHLORO-p-BENZOQUINONE WITH ACETOACETIC AND BENZOYLACETIC ESTERS

A. N. Grinev, Pan Bon-Khvar, V. N. Frosin and A. P. Terentyev

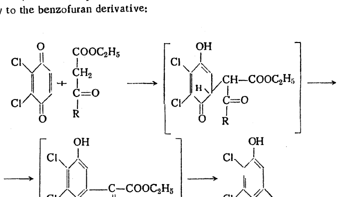
As was shown in our communications [1, 2], p-benzoquinone, toluquinone and α-naphthoquinone condense with acetoacetic and benzoylacetic esters, giving benzofuran, benzodifuran and naphthofuran derivatives. In studying the synthesis and properties of halo-substituted p-benzoquinone derivatives [3], we investigated here the condensation of chloro-p-benzoquinone and of 2, 3-dichloro-p-benzoquinone with the same ketoesters. The reaction was run by the earlier developed method in alcohol and in the presence of zinc chloride. For the chloroquinone the reaction proceeded in an excess of the ketoester for the most part by the general scheme:



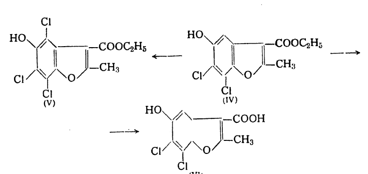
The structure of the diethyl ester of 4-chloro-2, 6-dimethyl-benzo(1, 2-b; 4, 5-b') difuran-3, 7-dicarboxylic acid (I) was shown by its conversion under chlorination into the diethyl ester of 4, 8-dichloro-2, 6-dimethylbenzo (1, 2-b; 4, 5-b') difuran-3, 7-dicarboxylic acid (II), obtained by a different method [4]. Saponification of the diethyl ester of 4-chloro-2, 6-dimethylbenzo (1, 2-b; 4, 5-b') difuran-3, 7-dicarboxylic acid gave the free acid (III):



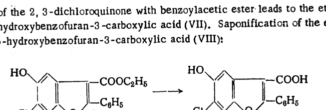
The reaction of the 2, 3-dichloro-p-quinone with either acetoacetic or benzoylacetic ester, as was to be expected, leads only to the benzofuran derivative:



As the result of condensing the 2, 3-dichloro-p-quinone with acetoacetic ester we obtained the ethyl ester of 6, 7-dichloro-2-methyl-5-hydroxybenzofuran-3-carboxylic acid (IV). The structure of this benzofuran derivative was shown by its conversion into the known [4] ethyl ester of 4, 6, 7-trichloro-2-methyl-5-hydroxybenzofuran-3-carboxylic acid (V). The ester (IV) was saponified with alcoholic caustic to 6, 7-dichloro-2-methyl-5-hydroxybenzofuran-3-carboxylic acid (VI):



The reaction of the 2, 3-dichloroquinone with benzoylacetic ester leads to the ethyl ester of 6, 7-dichloro-2-phenyl-5-hydroxybenzofuran-3-carboxylic acid (VII). Saponification of the ester gave the 6, 7-dichloro-2-phenyl-5-hydroxybenzofuran-3-carboxylic acid (VIII):



EXPERIMENTAL

1) Condensation of chloroquinone with acetoacetic ester. In a 3-necked flask fitted with reflux condenser and mechanical stirrer, upon heating, was dissolved 28 g zinc chloride in 28 g anhydrous alcohol. Into the resulting solution was run 39 g acetoacetic ester and at 80-90° in the course of 8-10 minutes was added 15 g chloroquinone in portions. The contents of the flask were heated about 30 minutes at 80°. After cooling the reaction mass, crystals formed and were separated, washed with a small amount of ether and dried. Yield 8,2 g. The crystals were recrystallized from alcohol. White crystals were obtained of the diethyl ester of 4-chloro-2, 6-dimethylbenzo-(1, 2-b; 4, 5-b')-difuran-3, 7-dicarboxylic acid (I). M. p. 164-165°. The ester was soluble in acetone, alcohol, dioxane; difficultly soluble in ether.

Found %: C 59.03, 59.07; H 5.07, 5.25. $C_{18}H_{17}O_6Cl$. Calculated %: C 59.27; H 4.70.

a) Chlorination of the diethyl ester of 4-chloro-2, 6-dimethylbenzo-(1, 2-b; 4, 5-b')-difuran-3, 7-dicarboxylic acid. 2 g of ester (I) was dissolved in acetic acid and into the resulting solution was passed chlorine at room temperature for 1 hour and 20 minutes. The reaction solution was heated with an excess of zinc dust and diluted with water. The crystals which came down were recrystallized twice from acetic acid. Yield 0.5 g of the diethyl ester of 4, 8-dichloro-2, 6-dimethylbenzo-(1, 2-b; 4, 5-b')-difuran-3, 7-dicarboxylic acid (II). M. p. 175° of the ester corresponded to the literature data [4].

b) Hydrolysis of the diethyl ester of 4-chloro-2, 6-dimethylbenzo-(1, 2-b; 4, 5-b')-difuran-3, 7-dicarboxylic acid. 4.2 g of ester (II) was added to a solution of 28 g caustic soda in 50 ml alcohol and the resulting suspension was heated 30 minutes on a water bath. The alcoholic solution of the acid salt was diluted with water, filtered and acidified with hydrochloric acid (Congo). The crystals of 4-chloro-2, 6-dimethylbenzo-(1, 2-b; 4, 5-b')-difuran-3, 7-dicarboxylic acid (III) that formed were recrystallized from acetic acid. M. p. of the acid above 240° (with decomp.).

Found %: C 54.06, 53.89; H 3.40, 3.31; Equiv. 308.8. $C_{14}H_9O_6Cl$. Calculated %: C 54.45; H 2.94; Equiv. 308.68.

2. Condensation of 2, 3-dichloroquinone with acetoacetic ester. The reaction was carried out as before. For reaction we took 2, 3-dichloroquinone 5 g, acetoacetic ester 18 g, zinc chloride 3.8 g and anhydrous ethyl alcohol 5 ml. Yield 2.9 g ethyl ester of 6, 7-dichloro-2-methyl-5-hydroxybenzofuran-3-carboxylic acid (IV). The ester was in the form of white crystals, m. p. 202.5° (from alcohol). Readily soluble in dichloroethane, dioxane, less – in alcohol and in ether.

Found %: C 49.85, 49.90; H 3.70, 3.77. $C_{12}H_{10}O_4Cl_2$. Calculated %: C 49.84; H 3.48.

a) Chlorination of the ethyl ester of 6, 7-dichloro-2-methyl-5-hydroxybenzofuran-3-carboxylic acid. 1 g of ester (IV) was dissolved in acetic acid and into this solution was passed chlorine for 1 hour and 20 minutes at room temperature; the solution was diluted with water; the crystals which formed were recrystallized twice from acetic acid. Crystals of the ethyl ester of 4, 6, 7-trichloro-2-methyl-5-hydroxybenzofuran-3-carboxylic acid (V) were separated, m. p. 138°, which corresponded to the literature data [4].

b) Hydrolysis of the ethyl ester of 6, 7-dichloro-2-methyl-5-hydroxylbenzofuran-3-carboxylic acid. Hydrolysis was carried out as before. For the experiment was taken 1.3 g of ester (IV), 1.5 g caustic soda, 18 ml alcohol. The acid was recrystallized from 50% acetic acid. The m. p. of 6, 7-dichloro-2-methyl-5-hydroxybenzofuran-3-carboxylic acid (VI) was above 275° (with decomp.). The acid was sparingly soluble in alcohol, ether, soluble in acetic acid.

Found %: C 46.13, 45.98, H 2.47, 2.66. $C_{10}H_6O_4Cl_2$. Calculated %: C 45.99, H 2.31.

3. Condensation of 2, 3-dichloroquinone with benzoyl acetate. The reaction was carried out as before. For the experiment was taken 6 g 2, 3-dichloroquinone, 7 g benzoyl acetate, 4.75 g zinc chloride and 6 ml ethyl alcohol. 5.35 g white crystals was separated from the mother liquor and had m. p. 185-186°

(from alcohol). From the mother liquor was isolated 3.8 g crystals with m. p. 185-186° (after two-fold recrystallization from alcohol). The obtained ethyl ester of 6, 7-dichloro-2-phenyl-5-hydroxybenzofuran-3-carboxylic acid (VII) was difficultly soluble in ether, alcohol, readily soluble in dichloroethane.

Found %: C 57.99, 57.86; H 3.65, 3.76. $C_{17}H_{12}O_4Cl_2$. Calculated %: C 58.15; H 3.45.

a) Hydrolysis of the ethyl ester of 6, 7-dichloro-2-phenyl-5-hydroxybenzofuran-3-carboxylic acid. Hydrolysis was carried out under the conditions of the preceding experiments. For the experiment was taken 2.3 g of ester (VII), 20 ml alcohol and 1.6 g caustic soda. Yield 1.94 g acid (VIII) with m. p. 207° (with decomp.). The acid was difficultly soluble in alcohol, acetone, soluble in acetic acid.

Found %: C 56.07, 56.12; H 2.35, 2.28. $C_{15}H_8O_4Cl_2$. Calculated %: C 55.78; H 2.49.

SUMMARY

Condensation of chloro-p-quinone and 2, 3-dichloro-p-quinone with acetoacetic and benzoylacetic esters gave heterocyclic compounds of the class of benzofuran and benzodifuran.

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REACTION OF HYDRAZINE DERIVATIVES

II. SYNTHESIS OF 1, 2, 3, 4, 5, 6, 7, 8 OCTAHYDROCARBAZOLE

A. N. Kost and I. I. Grandberg

In 1910 Piloty [1] found that diethyl ketone azine with excess anhydrous zinc chloride at 230° is converted into α, α'-diethyl- β, β'-dimethylpyrrole (25% yield). On heating desoxybenzoin azine at 180° in a hydrogen chloride stream G. Robinson and R. Robinson obtained tetraphenylpyrrole in 88% yield. On attempting to apply the Piloty method to cyclohexanone azine they isolated a compound having the composition $C_{12}H_{20}N_2 \cdot HCl \cdot ZnCl_2$, which when heated failed to show conversion into octahydrocarbazole [2]. Perkin [3] was able to achieve this synthesis (28% yield) by passing hydrogen chloride into a boiling mixture of cyclohexanone azine and tetralin. Later, Benary [4] observed that the reaction of either acetyl chloride or chloroacetyl chloride with cyclohexanone azine yields (in about 20% yield) the corresponding N-acyl derivative of octahydrocarbazole.

The reaction discovered by Piloty is apparently similar to Fischer's synthesis of indole compounds; consequently we, in accord with the data of A. E. Arbuzov [5], used traces of zinc chloride instead of an excess, and obtained from cyclohexanone azine (I) the octahydrocarbozole (II) in 79% yield. We were unable to extend the method to another azines – those of acetone, butyraldehyde, isovaleraldehyde, cyclopentanone, butyrone and acetophenone – which is in accord with the studies of other authors [1, 2, 6].

When the reaction was run with catalytic amounts of aniline hydrochloride we obtained the octahydrocarbazole in 19.7% yield, in which connection the main reaction product (61% yield) proved to be 1-cyclohexylcyclohexene (V). Similar results were obtained with quinoline hydrochloride. The use of acidic aluminosilicate catalyst gave 1-cyclohexylcyclohexene (in 39% yield) and a high-boiling substance, the composition of which was not investigated.

In elucidating the mechanism for the formation of the hydrocarbon it was revealed that aniline hydrochloride (when introduced in equimolar amounts) rearranges the cyclohexanone azine (I) into the pyrazoline base (III), which with the loss of nitrogen is easily converted into 1, 1-pentamethylene-bicyclo (0.1.4) heptane (IV) and then into 1-cyclohexylcyclohexene (V). These transformations (under different conditions) were described in our previous [7] communication *.

* After a description of the synthesis and transformations of 1, 1-pentamethylenebicyclo (0.1.4) heptane [7] had been sent to print there appeared a paper by Laber [8], who obtained this hydrocarbon from cyclohexylidenecyclohexanone through the pyrazoline base (without isolating the latter in pure form), opened the three-membered ring with either hydrogen chloride or hydrogen bromide (the same as we had done), and showed that this hydrocarbon under the influence of either hydrogen chloride or zinc chloride is isomerized to the cyclohexylcyclohexene in 55-64% yield. According to our data, isomerization under the influence of zinc chloride proceeds with tarring and gives a contaminated substance. If the reaction is run with aniline hydrochloride, then the yield of pure substance reaches 95.4%. Laber gives a density of 0.9015 for 1, 1-pentamethylenebicyclo(0.1.4)heptane; the other constants agree with ours. After repeated purification and trials we obtained d_4^{20} 0.9320. In our case the refraction and parachor are in good agreement with the theoretical values, while in the case of Laber a difference of 1.6 is observed for the refraction.

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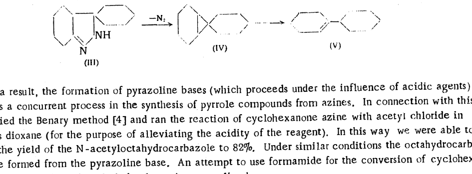

As a result, the formation of pyrazoline bases (which proceeds under the influence of acidic agents) appears as a concurrent process in the synthesis of pyrrole compounds from azines. In connection with this we modified the Benary method [4] and ran the reaction of cyclohexanone azine with acetyl chloride in anhydrous dioxane (for the purpose of alleviating the acidity of the reagent). In this way we were able to increase the yield of the N-acetyloctahydrocarbazole to 82%. Under similar conditions the octahydrocarbazole fails to be formed from the pyrazoline base. An attempt to use formamide for the conversion of cyclohexanone azine to the octahydrocarbazole led only to the pyrazoline base.

EXPERIMENTAL

1, 2, 3, 4, 5, 6, 7, 8-Octahydrocarbazole (II). In a 60 ml flask was placed 44.2 g freshly-distilled azine of cyclohexanone [7], 6 g glass wool and 0.15 g anhydrous zinc chloride; the reaction mixture was then heated with air condenser for 4 hours at 220-230° (thermometer in mixture) and without capillary was vacuum-distilled from the same flask. The colorless substance instantly crystallized in the condenser. Yield 32 g (79.3%) of octahydrocarbazone with b. p. 161.5-162.5° at 13 mm and m. p. 96°.

Found %: N 8.31, 8.42. $C_{12}H_{17}N$. Calculated %: N 8.00.

The substance very rapidly oxidized in air (after 20 minutes, m. p. 90°, after 90 minutes, m. p. 87°). It remained unchanged when kept in ampoules, sealed in a stream of ammonia. The acetyl derivative, obtained by boiling with acetic anhydride in the presence of perchloric acid, had m. p. 71° (from 75% alcohol). The literature data give b. p. 165-170° at 15 mm, m. p. 102° [3].

N-Acetyl-1, 2, 3, 4, 5, 6, 7, 8-octahydrocarbazole. To a solution of 19.2 g of freshly-distilled azine of cyclohexanone in 50 ml anhydrous dioxane, upon boiling, was added drop-wise 11.8 g acetyl chloride; a vigorous reaction took place, accompanied by the formation of ammonium chloride and greening of the mixture. The mixture was then boiled 30 minutes under reflux and after cooling, was poured in ice water. Yield 17.9 g (82.5%) N-acetyloctahydrocarbazole. After recrystallization from 75% aqueous methanol, it had m. p. 71°. Literature data give m. p. 73° [4].

Found %: N 6.81. $C_{14}H_{19}ON$. Calculated %: N 6.46.

The substance kept in air without noticeable oxidation. It gave no melting point depression with the substance prepared in the preceding experiment. In similar experiments with isovaleryl chloride, benzoyl chloride and benzenesulfochloride, a quantitative splitting out of ammonium chloride was noted; however, we could not purify the reaction products since they were obtained in the form of viscous liquids which decomposed upon vacuum-distillation.

Reaction of the azine of cyclohexanone with formamide. A mixture of 19.2 g azine of cyclohexanone and 5 g commercial formamide was heated. At 160° (thermometer in mixture) a vigorous evolution of ammonia started and stopped after 1.5-2 hours. After 3 hours of heating (160-190°) the reaction mass was vacuum-distilled (b. p. 144-203° at 10 mm). After prolonged standing (25-30 days) at −5°, a portion of the substance crystallized. Recrystallization from 50% methanol yielded 8.2 g (37.4%) N-formyl-3, 4-tetramethylene-5, 5-pentamethylenepyrazoline with m. p. 74°. It gave no melting point depression with the

previously prepared [7] substance, which had m. p. 73°. Hydrolysis of the mother liquor and the oil (boiling with concentrated hydrochloric acid for 0.5 hour) yielded 9.1 g (47.4%) of 3, 4-tetramethylene-5, 5-pentamethylenepyrazoline (III) with m. p. 63° (the azine of cyclohexane cleaved upon being boiled with concentrated hydrochloric acid and gave hydrazine dihydrochloride). The total yield (including the formyl derivative) was about 83%.

Reaction of the azine of cyclohexanone with other acidic agents. When a mixture of 38.4 g azine of cyclohexanone and 25.8 g aniline hydrochloride was heated, at 120-140° a very vigorous reaction began which had to be controlled by cooling the flask with water. When the reaction was complete, the cooled mixture was diluted to three times its original volume with ether; the crystals which came down were separated and dissolved in methanol; the addition of anhydrous ether brought down 5.1 g of ammonium chloride and after evaporation of the solvents, alkalization and distillation, we obtained 14.1 g pyrazoline base with b. p. 161-169° at 16-18 mm and m. p. 60°; its N-phenylcarbamide derivative had m. p. 122° (from alcohol). Literature data: b. p. 165° at 17 mm; m. p. 64° [9]; N-phenylcarbamide derivative: m. p. 122° [7], 124° [9]. From the basic ethereal layer was separated 12.1 g aniline and 2.9 g octahydrocarbazole with b. p. 154-160° at 10 mm, m. p. 89°.

When 38.4 g azine of cyclohexanone was heated with 2 g aniline hydrochloride, at 170° ammonia started to evolve. After heating the mixture for 3 hours at 210-230° and distillation, we obtained 6.9 g (19.7%) octahydrocarbazole with b. p. 150-158° at 10 mm and m. p. 90-91°, and 20 g of 1-cyclohexylcyclohexene (61%) with b. p. 235.5-236.5° at 746.3 mm, n_D^{20} 1.4949, d_4^{20} 0.9075. Literature data: b. p. 236° at 745 mm [7], 238° at 760 mm [10], n_D^{20} 1.4947 [8], 1.4948 [7], d_4^{20} 0.9040 [10], 0.9063 [7].

In a similar experiment with quinoline hydrochloride we obtained octahydrocarbazole in yield of 40.7% and 1-cyclohexylcyclohexene in yield of 44.6%. From 19.2 g azine and 2 g acid aluminosilicate catalyst (210-230°, 3.5 hours) we obtained 6.4 g (39%) of 1-cyclohexylcyclohexene and 10.1 g fraction with b. p. 295-310°, the composition of which was not investigated further. When a solution of 19.2 g azine of cyclohexanone in 50 ml methyl alcohol was run into a solution of 13.65 g anhydrous zinc chloride in 50 ml methyl alcohol, upon slight heating there came down 31.12 g of crystalline precipitate with m. p. 230-240° (decomp.). Analysis for nitrogen (Dumas) gave divergent results (from 7.12 to 10.07%). The same precipitate was obtained upon addition of methanolic solution of the azine to aqueous zinc chloride solution. Variation of pH of the aqueous solution did not bring down the complex compound. Acids resinified it and aqueous ammonia regenerated the azine. Heating to 250-300° did not cause the octahydrocarbazole to form. Similarly, in methanolic solution we obtained a complex compound of the azine of cyclohexanone with cuprous chloride of the composition $C_{12}H_{20}N_2 \cdot CuCl$. (Found %: N 9.68; Calculated %: N 9.62). In this case complex-formation is accompanied by considerable oxidation; the complex compound itself is not stable upon storage.

Decomposition of 3, 4-tetramethylene-5, 5-pentamethylenepyrazoline (III). Ammonia was bubbled for 3 hours into 16.4 g boiling pyrazolinic base. Fractionation yielded 5.8 g fraction with b. p. 180-200° at 10 mm, the composition of which was not investigated and 6.9 g (50.7%) 1, 1-pentamethylenebicyclo-(0.1.4)-heptane with b. p. 231-232° at 743 mm and n_D^{20} 1.4970.

After careful purification of 200 g of this hydrocarbon (washing with hot acetic acid solution of copper acetate, steam distillation, treatment for 3 hours at 20° with a solution of perbenzoic acid, washing with soda solution, partial oxidation with potassium permanganate and fractionation), we obtained the pure substance with b. p. 230.6° at 733.5 mm, n_D^{20} 1.4960, d_4^{20} 0.9320. Found MR_D 51.40; Calc. 51.71. Literature data: b. p. 98° at 12 mm [7], 108.5° at 18 mm [8]; 232° at 747 mm [7]; n_D^{20} 1.4966 [8], 1.4972 [7]; d_4^{20} 0.9015 (?) [8], 0.9278 [7]. Similarly from 16.4 g pyrazolinic base with 0.2 g anhydrous zinc chloride was obtained 8.3 g hydrocarbon with b. p. 230-235.5° at 742 mm and n_D^{20} 1.496 (a supposed mixture of spirane hydrocarbon with cyclohexylcyclohexene).

Isomerization of 1, 1-pentamethylenebicyclo-(0.1.4)-heptane (IV). 8.2 g of hydrocarbon and 0.5 g aniline hydrochloride were boiled for 5 hours, washed with 5% sulfuric acid, water, dried with potash and distilled. Yield 7.8 g (95.4%) 1-cyclohexylcyclohexene with b. p. 236.7-237.3° at 747.5 mm, n_D^{20} 1.4946, d_4^{20} 0.9069. When 16.4 g 1, 1-pentamethylenebicyclo-(0.1.4)-heptane was boiled (8 hours) with 0.2 g anhydrous zinc chloride, there was appreciable resinification. Fractions were obtained with b. p. from 230-237.5° at 744 mm, total weight 11.7 g, n_D^{20} 1.4966 (first fraction) and n_D^{20} 1.4957 (second fraction), the compositions of which were not investigated further.

SUMMARY

The transformations of cyclohexanone azine under the influence of acidic agents were investigated. Simple methods for the preparation of 1, 2, 3, 4, 5, 6, 7, 8-octahydrocarbazole and its N-acetyl derivative were described.

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HALOGENATION OF AROMATIC SILANES

I. PREPARATION AND PROPERTIES OF THE CHLORO DERIVATIVES OF PHENYLTRICHLOROSILANE

A. Ya. Yakubovich and G. V. Motsarev

If the preparation and properties of halogenated aliphatic silane derivatives, containing halogen atoms in the radical, having received quite detailed illumination in the literature [1], then the data with respect to the analogous halogenated aromatic silanes, as was already mentioned by us earlier [2, 3], is extremely meager. In connection with this we undertook a study of the halogenation of a number of aromatic silanes and of the properties of the resulting halogenated derivatives.

We began our study with phenyltrichlorosilane. Up to now not a single study, specially devoted to the halogenation of this silane, has appeared in the literature. We had already described earlier the preparation and properties of the bromo derivatives of phenyltrichlorosilane [2].

The chlorination of phenyltrichlorosilane, the same as its bromination, was run in the presence of the catalysts usually used in the halogenation of aromatic compounds (metallic iron [4], antimony trichloride, aluminum chloride [5] and iodine).

It was established that at 50-125°, with the proper molar ratios of phenyltrichlorosilane and chlorine, and using the mentioned catalysts, it is possible to obtain a whole series of chlorinated phenyltrichlorosilane derivatives, ranging from the monochloro- to the pentachloro-derivative, in 55-90% yields. In its intensity of reaction the chlorination of phenyltrichlorosilane in the presence of iodine differs sharply from that of chlorination in the presence of the other catalysts indicated above. The catalytic action of iodine becomes sufficiently effective only when the iodine is present in considerable amount. It should be mentioned that in the absence of catalysts the chlorination of phenyltrichlorosilane fails to proceed even at 170-180°.

A study of the chlorination of phenyltrichlorosilane revealed that depending on the nature of the catalyst used the substitution chlorination of the silane is accompanied to a greater or lesser degree by a parallel secondary process — destructive chlorination, proceeding with the formation of products that arise as the result of the silane molecule suffering cleavage at the C-Si bond *. This secondary reaction is observed to noticeable degree when the phenyltrichlorosilane is chlorinated in the presence of $AlCl_3$, and is present in very slight degree when this silane is chlorinated in the presence of $FeCl_3$ at 140-150° (cleavage is not observed at the lower temperature of 120-125°). The cleavage products of phenyltrichlorosilane when it is chlorinated in the presence of either $AlCl_3$ or $FeCl_3$ are, on the one hand, $SiCl_4$, and on the other, — chlorinated benzene derivatives. As a result, the chlorination of phenyltrichlorosilane proceeds by the scheme:

* The mechanism of this secondary process was examined by us in detail earlier [6].

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$$C_6H_{5-n}Cl_nSiCl_3 + Cl_2 \begin{cases} \longrightarrow C_6H_{4-n}Cl_{n+1}SiCl_3 + HCl & \text{(main reaction)} \\ \longrightarrow SiCl_4 + C_6H_{5-n}Cl_{n+1} & \text{(secondary reaction)} \end{cases}$$

The chlorination of phenyltrichlorosilane in the presence of either $SbCl_3$ or iodine fails to be accompanied by cleavage at the C-Si bond.

The influence of catalysts, of reactant ratios, and of temperatures on the results of chlorinating phenyltrichlorosilane are illustrated by the data given in the table:

Influence of Catalysts, Reactant Ratios and Temperatures On The Chlorination of Phenyltrichlorosilane

Exp. Nos.	Conditions for the chlorination of phenyltrichlorosilane				Composition of reaction products			
	Catalyst	Amount of catalyst (in % on the weight of silane taken)	Temperature	Mole ratio $C_6H_5SiCl_3 : Cl_2$	Unchanged silane (in %)	Chlorination products: Total yield (in %)	Chlorination products: Main reaction product	Amount of cleaved silane (in %)
1	Fe	0.5	60 – 70°	1 : 1.3	–	83.0	Mono-	–
2	Fe	0.5	60 – 70°	1 : 2.2	–	80.0	Di-	–
3	Fe	0.5	70 – 75	1 : 3.3	–	81.5	Tri-	–
4	Fe	0.5	110 – 125	1 : 6.5	–	84.6	Tetra- Penta-	–
5	$AlCl_3$	0.3	50 – 55	1 : 3.6	–	55.0	Tri-	43.0
6	$SbCl_3$	0.3	70 – 75	1 : 3.4	–	90.0	Tri-	–
7	I	0.75	50 – 75	1 : 4.0	72.0	9.5	Mono-	–
8	I	3.0	50 – 65	1 : 1.1	–	86.0	Mono-	–

All five chloro derivatives of phenyltrichlorosilane were isolated pure, and the physical and chemical characteristics for the di-, tri-, tetra- and pentachloro- derivatives are given here for the first time.

The chloro derivatives of phenyltrichlorosilane, with the exception of the pentachloro derivative, appear as colorless, mobile liquids that fume in the air (the tri- and tetrachloro- derivatives appear as oils). The pentachlorophenyltrichlorosilane is a white crystalline substance (slender needles), fuming in the air.

The boiling points and densities of the chlorinated phenyltrichlorosilane derivatives show steady increase in measure with increase in their chlorine content. All of the chlorophenyltrichlorosilanes are characterized by sharp odors, show vacuum-distillation without decomposition, and are readily soluble in most of the ordinary organic solvents.

To prove the structure of our synthesized chloro derivatives of phenyltrichlorosilane we used the reaction of their cleavage with either $AlCl_3$ or bromine water, the same as was used for the analogous bromo derivatives [2]. A study of the cleavage products of the chlorophenyltrichlorosilanes revealed that the cleavage of the latter with $AlCl_3$ yields the corresponding chloro derivatives of benzene, while when cleaved with bromine water (at elevated temperature, in a sealed tube) some of them yield chlorobromo derivatives of benzene

$$C_6H_{5-n}Cl_nSiCl_3 \begin{cases} \xrightarrow{+AlCl_3(H_2O)} C_6H_{6-n}Cl_n + SiO_2 + HCl \\ \xrightarrow{+Br_2(H_2O)} C_6H_{5-n}Cl_nBr + SiO_2 + HCl + HBr. \end{cases}$$

the structure of which can be judged from the positions of the chlorine atoms in the aromatic ring of the chlorophenyltrichlorosilane and from the orientation effect of the $SiCl_3$ group. It was established that despite the fact that the $SiCl_3$ group by its nature should show meta-orientation [7], the chlorination of phenyltrichlorosilane to the monochloro derivative in the presence of the above indicated catalysts leads to the exclusive formation of the para-chloro derivative. The formation of the para-, and not of the meta-chloro derivative, in the chlorination of phenyltrichlorosilane is supported both by the fact that the cleavage product of monochlorophenyltrichlorosilane with bromine water is p-chlorobromobenzene, obtained in 60% yield, and by the identity of the chlorination product with synthetic p-chlorophenyltrichlorosilane, obtained from p-ClC_6H_4MgBr and $SiCl_4$ [8]. Such a direction for this reaction indicated its anomalous behavior [7]. A study of the structure of the other chloro derivatives of phenyltrichlorosilane confirmed this postulation.

When we attempted to cleave dichlorophenyltrichlorosilane with bromine water it was revealed that this substance fails to react with bromine even under prolonged heating at 200-250°; consequently, to prove its structure the chloride was cleaved with $AlCl_3$ (with a 1 : 1 molar ratio of the reactants). After the reaction mass was decomposed with water the isolated cleavage product proved to be m-dichlorobenzene (40.0% yield), identified as the nitro derivative, which was shown to be 1-nitro-2, 4-dichlorobenzene. From this it follows that the described substance is 2, 4-dichlorophenyltrichlorosilane.

Similar to the dichloro derivative, trichlorophenyltrichlorosilane fails to be cleaved by bromine water (despite long heating in a sealed tube at 250°). The reaction product of trichlorophenyltrichlorosilane with $AlCl_3$ (1 : 1) proved to be 1, 3, 5-trichlorobenzene (37.0% yield). This indicates that the product obtained in the chlorination of phenyltrichlorosilane is the 2, 4, 6-trichloro derivative.

Since the trichlorophenyltrichlorosilane appears as a symmetrically substituted derivative, then the tetra- and penta- chlorophenyltrichlorosilanes are respectively the 2, 3, 4, 6-tetrachloro- and 2, 3, 4, 5, 6-pentachlorophenyltrichlorosilanes.

In the above description of the properties of the chlorinated phenyltrichlorosilanes special mention should be made of the peculiar behavior shown by these compounds toward bromine water. In measure with increase in the degree of chlorination of the phenyltrichlorosilane the cleavage of the C-Si bond by bromine is made more difficult. Thus, if phenyltrichlorosilane itself is cleaved at 100-110°, then the monochlorophenyltrichlorosilane already shows complete cleavage only at 140-150°, while the dichloro- and higher chlorinated derivatives fail to suffer cleavage even at 250°. As a result, based on their ease of cleavage with bromine (in the presence of water) these compounds can be arranged in the following order:

$$C_6H_5SiCl_3 > ClC_6H_4SiCl_3 > \ldots > C_6H_{5-n}Cl_nSiCl_3,$$

where $n = 2$ and more chlorine atoms.

Another peculiarity of this interesting reaction is the fact that the cleavage with bromine proceeds only in the presence of water; here dry bromine fails to react with phenyltrichlorosilane even at 140-150°. This peculiarity of the reaction could be explained by the fact that in the presence of water the phenyltrichlorosilane is first hydrolyzed to yield polysiloxanes, which are then cleaved by the bromine. However, attempts to cleave the earlier obtained dichlorophenylsiloxane resin with bromine (or bromine water) proved unsuccessful – cleavage failed to take place. It can be concluded from all of these observations that the cleavage of the C-Si bond with bromine water is a complicated process, in which the ions of hypobromous acid probably participate.

EXPERIMENTAL

I. Preparation of p-chlorophenyltrichlorosilane

1. Chlorination in the presence of iron. A stream of dry chlorine was passed for 40 minutes at the rate of 40 ml/min. at 60-70° into a mixture of 15.0 g phenyltrichlorosilane and 0.075 g powdered metallic iron (0.5% of the weight of phenyltrichlorosilane). The weight addition of the reaction mass after blowing through dry chlorine was 2.7 g (as against 2.5 necessary for chlorination to the monochloroderivative). Vacuum-distillation (7 mm) of the chlorination gave the following fractions: 1st, b. p. 70-80°, 0.2 g; 2nd, b. p. 80-90°,

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13.2 g; 3rd, b. p. 90-110°, 2.3 g. A second distillation of the 2nd fraction yielded 12.8 g liquid with b. p. 84-89° (7 mm), which was monochlorophenyltrichlorosilane. Yield 73.5%, based on the phenyltrichlorosilane taken for reaction.

Monochlorophenyltrichlorosilane was a colorless, mobile liquid, fuming in air, b. p. 87-88° at 7 mm; d_4^{20} 1.4062.

Found %: Cl (total) 57.2, 57.0; Cl (hydrolysis) 42.9, 42.8. $C_6H_4ClSiCl_3$. Calculated %: Cl (total) 57.7; Cl (hydrolysis) 43.29.

A side product of chlorination of phenyltrichlorosilane under the above described conditions was dichlorophenyltrichlorosilane, isolated from the 3rd fraction by a second distillation; we obtained 1.9 g liquid with b. p. 101-104° (7 mm). The total yield of chlorophenyltrichlorosilanes (mono- and dichloro-derivatives) was 83.0%.

By its properties, monochlorophenyltrichlorosilane proved identical to the p-chlorophenyltrichlorosilane prepared from $p\text{-}ClC_6H_4MgBr$ and $SiCl_4$. Moreover, to verify its structure the obtained monochlorophenyltrichlorosilane was subjected to cleavage with bromine water in a sealed tube. For this purpose 1.3 g monochlorophenyltrichlorosilane, 0.3 ml bromine and 2.0 ml water were placed in a glass tube. The tube was heated in a tube furnace at 140-160° for 7 hours. After heating, the contents of the tube were extracted with ether, the ethereal extract was washed with 10% soda solution, with water and was dried over $CaCl_2$. From the ethereal extract we isolated a white crystalline substance which after two recrystallizations from alcohol, yielded lustrous white crystals (flakes) with m. p. 65.5° and was p-chlorobromobenzene (~0.6 g). Yield ~60 %. A mixed sample with synthesized p-chlorobromobenzene gave no depression.

2. Chlorination in the presence of iodine. a) Into mixture of 10 g phenyltrichlorosilane and 0.075 g iodine (0.75% of the weight of phenyltrichlorosilane) was passed at 50-75° for 1 hour a stream of dry chlorine at the rate of 60 ml/min. 11.4 g chlorine was passed. In contrast to the preceding experiment, chlorination proceeded extremely sluggishly in this case (large chlorine by-pass). The weight addition of the reaction mass after blowing was 0.3 g (against 1.6 g, calculated for chlorination to the monochloro-derivative). Vacuum-distillation (7 mm) of the chlorination product yielded the following fractions: 1st, b. p. 69-80°, 8.0 g; 2nd, b. p. 80-98°, 1.4 g. The first fraction was unchanged phenyltrichlorosilane. From the second fraction we isolated 1.1 g of liquid with b. p. 87-89° (7 mm) and d_4^{20} 1.4071, which was monochlorophenyltrichlorosilane; yield 9.5%, based on the phenyltrichlorosilane taken for reaction.

b) Into a mixture of 15 g phenyltrichlorosilane and 0.5 g iodine (3% of weight of phenyltrichlorosilane) was passed at 50-65° for 1 hour a stream of dry chlorine at the rate of 60 ml/min.; 7.2 g of chlorine was passed. In this case there was a vigorous chlorination. The weight addition of the reaction mass after blowing was 2.5 g (as against 2.44 g necessary for chlorination to the monochloro derivative). Vacuum-distillation (7 mm) of the chlorination product yielded the following fractions: 1st, b. p. 70-80°, 1.0 g; 2nd, b. p. 80-95°, 12.0 g; 3rd, b. p. 95-112°, 3.5 g. A second distillation of the 2nd fraction yielded ~11.5 g monochlorophenyltrichlorosilane with b. p. 87-89° (7 mm) and d_4^{20} 1.4070, yield ~ 65%, based on the phenyltrichlorosilane taken for reaction. A side product of the reaction was dichlorophenyltrichlorosilane, which was isolated from the 3rd fraction by a second distillation; 2.6 g of liquid was also obtained with b. p. 102-104° (7 mm). The total yield of chlorophenyltrichlorosilanes was 86.0%. The obtained monochlorophenyltrichlorosilane by its constants proved identical to p-chlorophenyltrichlorosilane prepared by the chlorination of phenyltrichlorosilane in the presence of iron. Moreover, for complete proof of identity, the monochlorophenyltrichlorosilane was cleaved with bromine water by the above-described method and p-chlorobromobenzene was obtained in a yield of 60%, m. p. 66°.

II. Preparation of 2, 4-dichlorophenyltrichlorosilane

1. Chlorination of phenyltrichlorosilane in the presence of iron. Chlorination of phenyltrichlorosilane to the dichloro derivative was carried out under the same conditions as to the monochloro derivative; only the quantity of passed chlorine was correspondingly increased.

Into a mixture of 15 g phenyltrichlorosilane and 0.075 g powdered metallic iron (0.5% of weight of phenyltrichlorosilane) was passed at 70° for 1 hour and 45 minutes a stream of dry chlorine at the rate of 40 ml/min. 11.1 g of chlorine was passed. The weight addition of the reaction mass after blowing was 5.1 g (as against 4.9 g necessary for chlorination to the dichloro derivative). Vacuum-distillation (7 mm) of the chlorination product yielded the following fractions: 1st, b. p. 90-100°, 0.3 g; 2nd, b. p. 100-110°, 15.0 g, 3rd, b. p. 110-120°, 3.0 g. A second distillation of the 2nd fraction yielded 13.9 g of liquid with b. p. 101-105° (7 mm), which was dichlorophenyltrichlorosilane. Yield 70.0%, based on the phenyltrichlorosilane taken for reaction.

Dichlorophenyltrichlorosilane was a colorless, mobile liquid, fuming in air, b. p. 102-103° (7 mm), d_4^{20} 1.4820.

Found %: Cl (total) 62.4, 62.8; Cl (hydrolysis) 37.3, 38.5. $C_6H_3Cl_2SiCl_3$. Calculated %: Cl (total) 63.28; Cl (hydrolysis) 37.97.

A side product of the reaction was trichlorophenyltrichlorosilane, isolated from the 3rd fraction by a second distillation of the fraction; also 2.2 g of liquid was obtained, b. p. 117-119° (7 mm). The total yield of chlorophenyltrichlorosilanes was 80.0%.

For proof of structure of the obtained dichlorophenyltrichlorosilane, the latter was cleaved with $AlCl_3$. A mixture of 6.8 g silane and 3.25 g $AlCl_3$ was set aside at room temperature for 12 hours and then heated for 2 hours at 50-60° (the mixture set aside in a flask fitted with calcium chloride tube). The reaction mass was decomposed with cold water. After steam-distillation, extraction with ether and drying, the residue, after driving off the ether, was distilled on an oil bath. A liquid was thus obtained with b. p. 170-174° and d_4^{20} 1.2864, which corresponded in constants and chlorine content to m-dichlorobenzene. Yield 1.4 g, 40.0%, based on the silane taken for reaction.

Found %: Cl 48.0, 47.9. $C_6H_4Cl_2$. Calculated %: Cl 48.3.

For identification of m-dichlorobenzene (0.6 g), the latter was converted to the nitro derivative by a nitrating mixture. After two recrystallizations from alcohol, crystals (needles) were isolated which were 2, 4-dichloro-1-nitrobenzene with m. p. 32.2° (literature data: m. p. 31.5-33°). Yield ~ 61.5%, based on the m-dichlorobenzene taken for the reaction.

2. Chlorination of p-chlorophenyltrichlorosilane. Into a mixture of 5 g p-chlorophenyltrichlorosilane, prepared from $p\text{-}ClC_6H_4MgBr$ and $SiCl_4$ and 0.025 g powdered metallic iron (0.5% of weight of p-chlorophenyltrichlorosilane) was passed at 70° for 20 minutes a stream of dry chlorine at the rate of 40 ml/min. Two distillations of the chlorination product in vacuum yielded 4.1 g dichlorophenyltrichlorosilane, identified by b. p. 102-105° (7 mm) and density d_4^{20} 1.4823, as the 2, 4-dichloro derivative. Yield ~72.0 %, based on the p-chlorophenyltrichlorosilane taken for the reaction.

III. Preparation of 2, 4, 6-trichlorophenyltrichlorosilane.

1. Chlorination in the presence of iron. Into a mixture of 15 g phenyltrichlorosilane and 0.075 g powdered metallic iron (0.5%) was passed at 70-75° for 2 hours a stream of dry chlorine at the rate of 40 ml/min. 16.6 g of chlorine was passed. The weight addition of the reaction mass after blowing was 7.0 g (as against 7.3 g necessary for chlorination to the trichloro derivative). Distillation of the chlorination product in vacuum (4 mm) yielded the following fractions: 1st, b. p. 90-108°, 4.9 g; 2nd, b. p. 108-120°, 14.5 g; 3rd, b. p. 120-125°, 0.3 g. A second distillation of the 2nd fraction yielded 13.5 g of liquid with b. p. 112-114° (4 mm), which was trichlorophenyltrichlorosilane. Yield 60.4%, based on the phenyltrichlorosilane taken for reaction.

Trichlorophenyltrichlorosilane was a colorless, mobile, oily liquid, fuming in air, b. p. 117-118° (7 mm); d_4^{20} 1.5651.

Found %: Cl (total) 67.2, 67.0; Cl (hydrolysis) 33.4, 33.7. $C_6H_2Cl_3SiCl_3$. Calculated %: Cl (total) 67.62; Cl (hydrolysis) 33.81.

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A second distillation of the 1st fraction yielded 4.2 g dichlorophenyltrichlorosilane with b. p. 101-104° (7 mm). The total yield of chlorophenyltrichlorosilanes was 81.5%.

For proof of structure of the obtained trichlorophenyltrichlorosilane, the latter was cleaved with $AlCl_3$. For this a mixture of 2.7 g silane and 1.15 g $AlCl_3$ was kept for 8 hours at room temperature and then heated for 2 hours at 50-60° and decomposed with cold water. After steam-distillation, extraction with ether and drying, after the ether was driven off, the residue was in the form of white crystals (0.57 g), which after two recrystallizations from alcohol had m. p. 64° and in chlorine content corresponded to trichlorobenzene.

Found %: Cl 58.4, 58.5. $C_6H_3Cl_3$. Calculated %: Cl 58.6.

The isolated trichlorobenzene (yield ~ 37%, based on the silane taken for reaction) by melting point was identified as 1, 3, 5-trichlorobenzene (literature data: m. p. 63.4°).

2. Chlorination in the presence of $AlCl_3$. Into a mixture of 15 g phenyltrichlorosilane and 0.045 g $AlCl_3$ (0.3% of weight of phenyltrichlorosilane) was passed at 50-55° for 2 hours a stream of dry chlorine at the rate of 40 ml/min. 18.3 g of chlorine was passed. The weight addition of the reaction mass after blowing was 6.0 g. Moreover, in the receiver which was located at the outlet of the gases escaping from the reaction vessel and which was cooled externally with a freezing mixture (temperature −20°, −30°) was obtained 2.6 g of yellow, pungent liquid. Thus, the total weight addition of the reaction mass was 8.6 g (as against 7.3 g, necessary for chlorination to the trichloro derivative).

Distillation of the liquid in the receiver yielded a compound (2.0 g) with b. p. 56-57° and d_4^{20} 1.4823 which by constants was identified as $SiCl_4$. The distilled silicon tetrachloride was decomposed with water into hydrogen chloride and silicic acid. 0.6 g of SiO_2 (85.7%) was isolated. The quantity of hydrogen chloride was determined by titration with alkali; it corresponded to the yield of SiO_2.

Vacuum-distillation (7 mm) of the chlorination product yielded two fractions: 1st, b. p. 90-110°, 5.0 g; 2nd, b. p. 110-125°, 12.1 g.

When the first fraction was distilled, crystallization of the distillate was noted (crystals in the form of long needles). For investigation of composition, this fraction was treated with water and then steam-distilled. The aqueous distillate was extracted with ether and the ethereal solution was dried. After driving off the ether, the residue was in the form of white crystals (3.0 g) which after 2 recrystallizations from alcohol had m. p. 115-125° and corresponded in chlorine content to tetrachlorobenzene.

Found %: Cl 65.2, 65.4. $C_6H_2Cl_4$. Calculated %: Cl 65.7.

The indefinite melting temperature of the crystals indicated that they were, evidently, a mixture of isomeric tetrachlorobenzenes with a predominance of the 1, 2, 4, 5-tetrachloro derivative (m. p. 137-138°). After steam-distillation, the residue (~1.0 g) was a transparent light-yellow resin, the composition of which was shown by analysis to be $(C_6H_3Cl_2SiO_{1.5})_n$.

Found %: Cl 35.5, 35.6; Si 14.5, 14.1. $(C_6H_3Cl_2SiO_{1.5})_n$. Calculated %: Cl 35.85; Si 14.1.

Thus, the 1st fraction contained chiefly tetrachlorobenzene and some dichlorophenyltrichlorosilane.

A second distillation of the 2nd fraction yielded 11.0 g of liquid with b. p. 118-120° (8 mm), which was trichlorophenyltrichlorosilane (d_4^{20} 1.5657). The total yield of chlorophenyltrichlorosilanes was 55%.

3. Chlorination in the presence of $SbCl_3$. Into a mixture of 15 g phenyltrichlorosilane and 0.045 g $SbCl_3$ (0.3% of weight of phenyltrichlorosilane) was passed at 75° for 2 hours a stream of dry chlorine at the rate of 40 ml/min. 17.0 g of chlorine was passed. The weight addition of the reaction mass after blowing was 7.8 g (as against 7.3 g necessary for chlorination to the trichloro derivative). Distillation of the chlorination product in vacuum (7 mm) yielded the following fractions: 1st, b. p. 90-110°, 0.5 g; 2nd, b. p. 110-125°, 16.7 g; 3rd, b. p. 125-135°, 3.3 g. A second distillation of the 2nd fraction yielded 15.0 g of liquid with b. p. 118-120° (8 mm) and d_4^{20} 1.5654, which was trichlorophenyltrichlorosilane. A second distillation of the 3rd fraction yielded 2.6 g tetrachlorophenyltrichlorosilane with b. p. 130-132° (7 mm). The total yield of chlorophenyltrichlorosilanes was ~90.0%.

IV. Preparation of 2, 3, 4, 6-tetrachlorophenyltrichlorosilane and pentachlorophenyltrichlorosilane. Into a mixture of 15 g phenyltrichlorosilane and 0.075 g powdered metallic iron (0.5%) was passed a stream of dry chlorine at the rate of 40 ml/min., first for 2 hours at 100° and then for 2 hours and 20 minutes at 120-125°. 32.3 g chlorine was passed. The weight addition of the reaction mass after blowing was 11.4 g (as against 12.2 g necessary for chlorination to the pentachloro derivative). As the chlorination product cooled it crystallized (long needles). Vacuum-distillation yielded fractions: 1st, b. p. 120-130° (4 mm), 7.0 g; and 2nd, b. p. 140-155° (9 mm), 17.0 g.

A second distillation of the 1st fraction yielded 6.4 g of liquid with b. p. 124-127° (4 mm) which was tetrachlorophenyltrichlorosilane. Tetrachlorophenyltrichlorosilane was a colorless, mobile, oily liquid, fuming in air, b. p. 125-126° (4 mm); d_4^{20} 1.6340.

Found %: Cl (total) 70.8, 70.5; Cl (hydrolysis) 30.5, 30.3. $C_6HCl_4SiCl_3$. Calculated %: Cl (total) 71.1; Cl (hydrolysis) 30.47.

A second distillation of the 2nd fraction yielded 16.0 g of colorless transparent liquid with b. p. 144-149° (8 mm), which upon cooling crystallized into long white needles which were pentachlorophenyltrichlorosilane. Yield 58.8%, based on the phenyltrichlorosilane taken for reaction.

Pentachlorophenyltrichlorosilane was a white crystalline substance, difficultly soluble in ether and in benzene, readily soluble in carbon tetrachloride and in chlorobenzene; does not burn when placed in bare flame. It crystallized from a mixture of carbon tetrachloride and ether in the form of needles, m. p. 59.5°, b. p. 146-147° (8 mm).

Found %: Cl (total) 73.4, 73.1; Cl (hydrolysis) 27.1, 27.3. $C_6Cl_5SiCl_3$. Calculated %: Cl (total) 73.96; Cl (hydrolysis) 27.73.

The total yield of polychlorophenyltrichlorosilanes was 84.6%.

SUMMARY

1. It was established that the chlorination of phenyltrichlorosilane in the presence of the usual catalysts for the halogenation of aromatic compounds ($FeCl_3$, $AlCl_3$, $SbCl_3$, I_2) can give a whole series of chlorinated phenyltrichlorosilane derivatives, ranging from the monochloro- to the pentachloro- derivative.

2. It was observed, in contrast to chlorination in the presence of either $SbCl_3$ or iodine, that the chlorination of phenyltrichlorosilane in the presence of $AlCl_3$ is accompanied by a sharply defined secondary process, which proceeds with the formation of products that arise as the result of cleavage of the silane molecule at the C-Si bond by chlorine. This secondary process of destructive chlorination proceeds to very slight degree in the presence of $FeCl_3$ when phenyltrichlorosilane is chlorinated at 140-150° to the pentachloro- derivative.

3. All five chloro derivatives of phenyltrichlorosilane were isolated in the pure form, and the physicochemical and chemical properties of the previously unknown di-, tri-, tetra- and pentachloro-derivatives were characterized for the first time.

4. The structure of all five chlorination products of phenyltrichlorosilane was shown, and it was established that the monochloro- derivative is the 1, 4-isomer, the dichloro- derivative – the 1, 2, 4-isomer, the trichloro- derivative – the 1, 2, 4, 6-isomer, the tetrachloro- derivative – the 1, 2, 3, 4, 6-isomer, and the pentachloro- derivative – the 1, 2, 3, 4, 5, 6-pentachlorophenyltrichlorosilane.

5. It was revealed that the chlorination of phenyltrichlorosilane in the presence of any of the above mentioned catalysts proceeds abnormally with respect to the orientation effect of the $SiCl_3$ group. Instead of normal meta-orientation, here anomalous ortho-, para-orientation of the chlorine atoms entering the ring is observed.

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SYNTHESIS OF PHYSIOLOGICALLY ACTIVE PUTRESCINE DERIVATIVES

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Pharmacological study of earlier synthesized N-alkylated putrescines has shown that these substances possess clearly defined hypotensive properties. The degree and duration of reduction in blood pressure is in inverse proportion to the size of the radicals: N, N'-diisopropylputrescine is the most active, while the mono- and N, N'-diisooctylputrescines are the least active in hypotensive effect for the given series of substances. All of the studied alkylated diamines depress the central nervous system and block the sympathetic ganglia.

It seemed of interest to obtain those substances in which the ability to stimulate the central nervous system is combined with hypotensive properties. For this purpose we synthesized two new substances: di-N, N'-(1-benzylethyl) putrescine (I) and N-isopropyl-N'-(1-benzylethyl) putrescine (II).

$$C_6H_5-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH-(CH_2)_4-NH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C_6H_5 \qquad (I)$$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH-(CH_2)_4-NH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C_6H_5 \qquad (II)$$

The first of these substances can be regarded as being a substituted diisopropylputrescine derivative, expected to show the hypotensive effect characteristic of the latter. Together with this, two phenamine (1-benzylethylamine) molecules are combined in the structure of this diamine, bound through nitrogen atoms to the chain of methylene groups. Phenamine and its N-derivatives are extremely active stimulators, and it could be expected that di-N, N'-(1-benzylethyl) putrescine will also show the same characteristic physiological action. Pharmacological study confirmed this postulation; however, it was revealed that di-N, N'-(1-benzylethyl) putrescine possesses less prolonged hypotensive effect than does diisopropylputrescine, fails to show any ganglion-blocking properties, while its nerve stimulatory activity is weaker than that of phenamine. As was to be expected, the physiological properties of N-isopropyl-N'-(1-benzylethyl)-putrescine lie intermediate between those of di-N, N'-(1-benzylethyl) putrescine and N, N'-diisopropylputrescine.

We obtained di-N, N'-(1-benzylethyl) putrescine by the reductive alkylation of putrescine with methyl benzyl ketone (50% yield). The unsymmetrical substitution of putrescine in the synthesis of the second diamine was run in two stages: 1) the reductive alkylation of putrescine with an equimolar amount of acetone (the yield of isopropylputrescine was 46%), and 2) the condensation of isopropylputrescine with methyl benzyl ketone and subsequent hydrogenation of the reaction mixture (73% yield). The alkylation of both amino groups was proved by reaction with nitrous acid, where nitrogen evolution failed to occur.

Desiring to elucidate the preparative significance of the reductive alkylation method for obtaining monosubstituted diamines, we repeated the earlier synthesis of isoamylputrescine and obtained this substance in 51% yield. In some of the experiments on the preparation of monosubstituted putrescines we added, prior to hydrogenation, an equimolar amount of hydrochloric acid with respect to the amount of putrescine taken. This partial

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neutralization of the putrescine failed to change the yield of monosubstituted putrescine and did not affect the hydrogenation rate.

EXPERIMENTAL

N, N'-di-(1-benzylethyl)-putrescine (I). A solution of 0.038 mole (3.8 ml) putrescine * and 0.078 mole (10.5 g) methylbenzyl ketone in 10 ml alcohol was hydrogenated with platinum black prepared from 0.18 g platinic oxide. 1.65 liters of hydrogen was absorbed (calculated 1.75 liters). The solution, freed from platinum, was neutralized with an alcoholic solution of hydrogen chloride. The dihydrochloride was repeatedly recrystallized from water. Yield 0.019 mole (7.4 g) of dihydrochloride; yield 50%. M. p. 285-286°. The HCl content of the dihydrochloride was determined gravimetrically.

Found %: HCl 18.32. $C_{22}H_{34}N_2Cl_2$. Calculated %: HCl 18.35.

The dipicrate, recrystallized from alcohol, melted at 187.5-188.5°.

Found %: C 52.12; H 5.16; N 14.74. $C_{34}H_{38}O_{14}N_8$. Calculated %: C 52.17; H 4.89; N 14.32.

Isopropylputrescine. 1) A solution of 0.149 mole (15 ml) putrescine, 0.158 mole (11.6 ml) acetone, 0.149 mole hydrogen chloride and 25.5 ml water ** in 100 ml alcohol was hydrogenated with platinum black prepared from 0.82 g platinic oxide. 3.06 liters hydrogen was absorbed in the course of 210 minutes (calculated 3.54 liters). After separating the platinum from the solution, the solvent was driven off and the bases were liberated by addition of alkali and then vacuum-distilled. Yield 0.0690 mole (8.98 g) of isopropylputrescine which distilled at 103.0-104.2° (60 mm); yield 46%.

2) The experimental conditions and the quantities of substances were the same but in place of hydrochloric acid, an equal quantity of water was added. Hydrogenation was complete after 210 minutes. 3.17 liters of hydrogen was absorbed (calculated 3.54 liters). Yield 0.0686 mole (8.93 g) of isopropylputrescine with b. p. 102.6-102.8° (58 mm), d_4^{20} 0.8370; yield 46%.

The dihydrochloride, m. p. 177-178° and the dipicrate, m. p. 163.5-164.5° were obtained.

Analysis of the dipicrate. Found %: N 19.23. $C_{19}H_{24}O_{14}N_8$. Calculated %: N 19.04.

N-isopropyl-N-(1-benzylethyl)-putrescine (II). A solution of 0.115 mole (15 g) isopropylputrescine, 0.127 mole (17 g) methylbenzyl ketone in 50 ml alcohol was hydrogenated with platinum black prepared from 1 g platinic oxide. 2.29 liters of hydrogen was absorbed in the course of 315 minutes (calculated 2.84 liters). After removal of the catalyst and driving off the solvent, the mixture was vacuum-distilled. Yield 0.0835 mole (20.74 g) of base which distilled at 152-152.6° (6 mm), $d_4^{20.7}$ 0.9082; yield 73%.

Found %: C 77.40, 77.61; H 11.38, 11.32; N 11.23, 11.31. $C_{16}H_{28}N_2$. Calculated %: C 77.36; H 11.36; N 11.28.

The dihydrochloride, recrystallized from alcohol, melted at 218-218.5° and did not give off nitrogen in reacting with nitrous acid. The picrate had m. p. 168-168.5° (from alcohol).

N-isoamylputrescine. In one of the experiments a mixture of 0.050 mole (5 ml) putrescine, 0.05 mole hydrogen chloride, 7.35 ml water and 0.056 mole (6.1 ml) of isovaleric aldehyde in 55 ml of alcohol was hydrogenated in the presence of platinum black prepared from 0.5 g platinic oxide. In the course of 100 minutes, 1.17 liters of hydrogen was absorbed (calculated 1.25 liters). After removal of the platinum and alcohol, the reaction mixture was treated with alkali and the free bases were extracted with ether. The substance obtained in 4 identical experiments was vacuum-distilled. Yield 0.103 mole (16.34 g) of isoamylputrescine which boiled in the range of 89.4-90.4° (6 mm) and at 93.2-94.6° (8 mm) (the literature gives 95-96° at 10 mm); yield 51%. The dipicrate of this base melted at 173-174°, the dihydrochloride at 292°. Both salts were identified with the corresponding salts of isoamylputrescine which were previously prepared [1].

* The putrescine was fused before the experiment.

** A quantity sufficient to dissolve the putrescine hydrochloride.

SUMMARY

For the purpose of obtaining substances, showing combined hypotensive and nerve stimulatory properties, we synthesized two new compounds: di-N, N'-(1-benzylethyl) putrescine (I) and N-isopropyl-N'-(1-benzylethyl) putrescine (II). Both substances are considerably less active stimulants than is phenamine, and show less prolonged hypotensive action than does N, N'-diisopropylputrescine.

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FRITILLARIA ALKALOIDS

I. ALKALOIDS OF FRITILLARIA RADDEANA RGL.

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One of us together with Lazuryevsky [1, 2] has shown that the bulbs of F. Raddeana (local name "alvan") contain a considerable amount of alkaloids. From the total alkaloids found here we isolated a new crystalline base, which we named raddeanine, having m. p. 255-257° and empirical formula $C_{21}H_{33}(\equiv N)(OH)_2$. In this communication we give the results obtained by us in separating the whole alkaloidal mixture.

The plant bulbs for our work were harvested in 1952 near the Kara-Kala station in Turkmen SSR in the early part of May and toward the end of July. It was found that the plants that were harvested in May had a higher alkaloidal content (0.85-0.90%) than did those that were harvested in July (0.70-0.75%). It is interesting to mention that the content of the main alkaloid, raddeanine, in the total alkaloids was greater in July (64%) than it was in May (42%). This shows the considerable changes present in the composition of the alkaloids and in their total amount in the plant as a function of the vegetation period.

The total alkaloidal content was isolated in the usual manner: extraction with dichloroethane, washing the dichloroethane extract with 10% sulfuric acid, and precipitation of the alkaloids as a yellow powder from acid solution with ammonia. Repeated recrystallization of the mixed alkaloids from alcohol and washing with acetone enabled us to obtain raddeanine with m. p. 265-266°.

Raddeanine is a saturated tertiary base and fails to contain the N-methyl group. It is optically inactive. It gives a number of well-crystallizing salts and derivatives (Table 1). The analytical data for raddeanine itself, as well as for its salts and derivatives, in contrast to the original formula [2], show good agreement with the formula $C_{24}H_{37}(\equiv N)(OH)_2$. The hydroxyls in raddeanine appear as alcohol groups; depending on the conditions, they behave differently when acylated. When reacted with acetyl chloride in the cold the monoacetyl derivative is obtained, while diacetylraddeanine is obtained when the mixture is heated. The heating of raddeanine with benzoic anhydride yields the monobenzoyl derivative. Reaction with benzoyl chloride, in the presence of pyridine, leads to dibenzoylraddeanine, which when saponified with 45% sulfuric acid again reverts back to raddeanine.

From the acetone and alcohol mother liquors, after removal of the raddeanine and prolonged treatment, we isolated 5 more new crystalline alkaloids (Table 2).

TABLE 1

Salts and Derivatives of Raddeanine.

	Melting point	Composition	Analytical results
Hydrochloride	170-171°	$C_{24}H_{39}O_2N \cdot HCl$	Found %: N 3.39, 3.25; Cl 8.70, 8.75. M 408.1, 405.7. Calculated %: N 3.42; Cl 8.64. M 409.5.
Perchlorate	206-207	$C_{24}H_{39}O_2N \cdot HClO_4$	Found %: N 2.80, 2.94. Calculated %: N 2.95.
Methiodide	250-252	$C_{24}H_{39}O_2N \cdot CH_3I$	Found %: N 2.85, 2.79; I 24.62, 24.55. Calculated %: N 2.72, I 24.66.
Chloroaurate	130-132	–	–
Monoacetyl derivative	115-116	$C_{26}H_{41}O_3N$	Found %: C 75.34, 75.63, 75.18; H 10.13, 10.08, 10.28; N 3.38, 3.51. Calculated %: C 75.19; H 9.88; N 3.37.
Diacetyl derivative	172-174	$C_{28}H_{43}O_4N$	Found %: C 73.23, 73.18; H 9.55, 9.66; N 3.13, 3.20. Calculated %: C 73.52; H 9.41; N 3.06.
Monobenzoyl derivative	236-237	$C_{31}H_{43}O_3N$	Found %: C 77.98, 77.87; H 9.10, 9.25; N 2.85, 2.91. Calculated %: C 77.98; H 9.02; N 2.93.
Dibenzoyl derivative	190-192	$C_{38}H_{47}O_4N$	Found %: N 2.21, 2.30. Calculated %: N 2.41.

EXPERIMENTAL

Isolation of total alkaloids. Isolation of the alkaloids was performed by the usual method; from 7.5 kg of bulbs harvested in May 60 g of alkaloids was isolated and from the same amount of bulbs collected in July we isolated 47 g.

Resolution of total alkaloids obtained from bulbs harvested in May. 60 g total alkaloids was repeatedly recrystallized from alcohol; the crystals so obtained were recrystallized from alcohol; the crystals then had m. p. 257-259° (with decomp.) and weighed 14 g. The crystals were washed with acetone in the cold, separated and repeatedly recrystallized from alcohol. The crystals thus obtained were thoroughly homogeneous crystals of raddeanine in the form of colorless prismatic needles with m. p. 265-266°. From the alcoholic mother liquors, after driving off the alcohol and treatment with acetone, was obtained 2 g more of raddeanine with m. p. 256-259°.

In the acetonic mother liquors, after driving off the solvent, a yellowish powder remained which was dissolved in 10% hydrochloric acid and precipitated with ammonia in the form of a colorless powder (40 g). The powder was treated with petroleum ether with heating. After the solvent had been driven off until a small volume of solution remained, cooling brought down 0.3 g of crystals. The crystals were separated, washed and recrystallized from petroleum ether. Colorless crystals were obtained with m. p. 245-247° (with decomp.) ("Base No. 5"). A mixed sample with raddeanine melted at 234-236°.

TABLE 2

New Alkaloids Isolated from Fritillaria Raddeana Rgl.

	Content in total alkaloids (in %)	Melting point	Composition	Analytical results
Raddeamine	1.83	271-272°	$C_{23}H_{37}O_2N$	Found %: C 76.64, 76.54; H 10.40, 10.47; N 3.95, 3.87. Calculated %: C 76.88; H 10.31; N 3.90.
Raddeamine hydrochloride	–	235-236	$C_{23}H_{37}O_2N \cdot HCl$	Found %: Cl 9.14, 9.09. M 388.5, 390.4. Calculated %: Cl 8.98; M 395.5.
Alvanine	1.3	185-187	$C_{26}H_{43}O_3N$	Found %: C 74.74, 74.61; H 10.39, 10.54; N 3.45, 3.45. Calculated %: C 74.83; H 10.31; N 3.36.
Alvanine hydrochloride	–	163-165	$C_{26}H_{43}O_3N \cdot HCl$	Found %: Cl 7.86, 8.09. M 453.8, 451.6. Calculated %: Cl 7.83. M 453.5.
Alvanidine	1.33	235-236	$C_{20}H_{33}O_2N$	Found %: C 75.34, 74.87; H 10.40, 10.51; N 4.31, 4.35. Calculated %: C 75.23; H 10.34; N 4.39.
Alvanidine hydrochloride	–	174-175	$C_{20}H_{33}O_2N \cdot HCl$	Found %: Cl 9.98, 10.10; M 355.8, 351.6. Calculated %: Cl 9.99; M 355.5.
Base No. 5	0.5	245-247	–	–
Hydrochloride of Base No. 6	–	197-199	–	–

After treatment with petroleum ether, the residue was extracted with benzene for 20 hours in a continuous extraction apparatus. From the portion insoluble in benzene (26 g), after removal of resins (by repeatedly washing with acidic chloroform solution), precipitation of the alkaloids with ammonia solution yielded a yellow powder. The latter was dissolved in chloroform, extracted with 5% hydrochloric acid solution and precipitated with 15% ammonia solution. Three repetitions of this operation and recrystallization from alcohol yielded raddeanine with m. p. 258-260° (4 g). From the alcoholic mother liquor, after removal of the solvent, was obtained a pale-yellow powder (14 g), which was very readily soluble in all ordinary organic solvents. Individual substances could not be isolated from it. Evaporation of the benzene from the benzene extract yielded a brownish-yellow powder (12 g). The powder was dissolved in 7% hydrochloric acid and precipitated with ammonia. The precipitate was boiled with benzene (4 times with 35-ml portions). The portion soluble in benzene (4 g) was a yellowish powder which was treated with cold acetone and the residue was recrystallized from alcohol; 2 g of raddeanine was thus obtained with m. p. 259-260°. The acetonic mother liquor was concentrated to low bulk and set aside overnight; crystals came down (1.1 g) which, after two recrystallizations from acetone, had m. p. 271-272° (raddeamine). A mixed sample with raddeanine melted at 227-229°. A mixture with "Base No. 5" melted at 235-238°.

After boiling with benzene, the residue was treated at the boil with a mixture of acetone and methyl alcohol. Upon standing, crystals came down from the solution. After two recrystallizations from alcohol, raddeanine was obtained with m. p. 254-260° (3 g).

The portion which was insoluble in a methanol-acetone mixture was dissolved with heating in ethyl alcohol; after evaporation of the alcohol to low bulk and prolonged standing at room temperature, crystals (0.8 g) came down from the solution and after 2 recrystallizations from alcohol, had m. p. 235-236° (alvanidine). A mixed sample with raddeanine melted at 230-232°. A mixture of alvanidine and raddeamine melted at 231-234°. In mixture with "Base No. 5", alvanidine melted at 221-224°. From the alcoholic mother liquors, no crystalline bases could be obtained.

Resolution of total alkaloids obtained from bulbs harvested in July. From 50 g total alkaloids by means of recrystallization from alcohol, 27 g of raddeanine was isolated with m. p. 259-260°, which after suitable treatment yielded raddeanine with m. p. 265-266°. The mother liquors were combined after separation of raddeanine and the solvents were driven off. The residue was dissolved in 7% sulfuric acid and precipitated with ammonia in the form of a colorless powder. The latter was boiled several times with petroleum ether. The petroleum ether was driven off until the residue was dry and the latter was treated with 5% hydrochloric acid solution; almost half of the mass (0.45 g) remained insoluble in the form of the hydrochloride, which after recrystallization from water melted at 197-199° ("Base No. 6"). From the acidic solution, upon neutralization with 15% ammonia, an amorphous powder (0.3 g) came down, m. p. 165-172° (with decomp.); it could not be obtained in its crystalline state.

After treatment with petroleum ether, the residue was boiled several times with benzene. From the benzene solution, after driving off the solvent until a small volume remained, upon standing, crystals (3 g) came down which upon recrystallization from alcohol, yielded raddeanine with m. p. 259-260°. The benzene mother liquor, after separation of crystals, was evaporated to dryness and treated with cold acetone. From the portion which was insoluble in acetone was obtained raddeanine, m. p. 256-259° (2 g) by recrystallization from alcohol. After driving off the solvent until a small volume remained, long standing (for a month) gave crystals (0.65 g) which after recrystallization from acetone had m. p. 185-187° (alvanine). From the portion which was insoluble in boiling benzene (12 g) and which was in the form of a brown powder, no crystalline bases could be obtained.

Raddeanine was readily soluble in chloroform and in dichloroethane, more difficultly soluble in alcohol and in acetone, very difficultly soluble in benzene and insoluble in water, ether, in alkali and ammonia solutions. It could not be hydrogenated with hydrogen in the presence of Ni and Pt or with sodium in alcohol. For analysis, raddeanine was taken with m. p. 265-266°, vacuum-dried (1 mm) at 80-90° for 2 hours.

Found %: C 77.18, 77.13; H 10.30, 10.40; N 3.78, 3.86; OH 8.29, 8.45. $C_{24}H_{37}(OH)_2N$. Calculated %: C 77.21; H 10.46; N 3.75; OH 9.12.

Raddeamine. It was in the form of crystals, m. p. 271-272°. It was readily soluble in chloroform, dichloroethane and in alcohol, more difficultly – in acetone, and insoluble in ether and in water. It gave only the crystalline hydrochloride.

Raddeamine hydrochloride. 5 ml of 5% hydrochloric acid solution was added to 0.1 g of base and the total mass was steamed to dryness on a water bath. The dry residue was first recrystallized from water and then from alcohol; crystals were obtained with m. p. 234-235°. The hydrochloride was difficultly soluble in water, more readily in alcohol, and practically insoluble in acetone.

Alvanine. Coarse lustrous crystals with m. p. 185-187°. It was readily soluble in chloroform and in dichloroethane, sparingly in acetone, insoluble in ether, water and in petroleum ether. It gave a hydrochloride which crystallized well.

Alvanine hydrochloride. The base was dissolved in alcohol and to this was added an alcoholic solution of hydrogen chloride until an acid reaction was obtained on Congo. The alcohol was driven off on a water bath until a dry residue remained. The dry residue was recrystallized from anhydrous alcohol; crystals came down with m. p. 163-165°.

Alvanidine. The base was in the form of white granular crystals with m. p. 235-236°. It was readily soluble in chloroform and in dichloroethane, more sparingly soluble in methyl and ethyl alcohols, very sparingly soluble in acetone, and practically insoluble in ether and in water. It gave a hydrochloride which crystallized well.

Alvanidine hydrochloride. 0.05 g base was dissolved in 5 ml alcohol and to this was added an alcoholic solution of hydrogen chloride until an acid reaction was obtained on Congo. After evaporating off the alcohol in vacuum, a white powder remained which after recrystallization from a mixture of anhydrous alcohol and dry acetone had m. p. 174-175°.

SUMMARY

1. The bulbs of F. Raddeana, harvested in May, have a higher alkaloidal content (0.85-0.90%) than do those that were harvested in July (0.70-0.75%).

2. The amount of raddeanine in the total alkaloids varies as a function of the harvesting season. The bulbs of the plants harvested in May, contain only 42% raddeanine; those that were harvested in July of the same year show a raddeanine content of 64%, based on the total amount of alkaloids.

3. In addition to raddeanine, 3 new crystalline alkaloids were isolated from the bulbs, for which the empirical formulas were determined: raddeamine $C_{23}H_{37}O_2N$, alvanine $C_{26}H_{43}O_3N$, and alvanidine $C_{20}H_{33}O_2N$, and also "Base No. 5" with m. p. 245-247°, and "Base No. 6" (isolated as the hydrochloride). As a result, it was established that the bulbs of F. Raddeana contain, besides raddeanine, at least five other alkaloids.

4. The earlier found empirical formula for raddeanine was corrected. It was shown that it has the composition $C_{24}H_{39}NO_2$.

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HEXAALKYLDISILANES

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Based on existing literature data the synthesis of hexaalkyldisilanes R_3SiSiR_3 (R = alkyl) can be realized by two paths: a) the reaction of hexahalodisilanes with either organozinc or organomagnesium compounds [1-5] in accord with the scheme:

$$Si_2X_6 \xrightarrow{+6RMgX} Si_2R_6 + 6MgX_2$$

$$Si_2X_6 \xrightarrow{+3ZnR_2} Si_2R_6 + 3ZnX_2$$

and b) the reaction of trialkylhalosilanes with metallic sodium in the absence of solvent [6, 7] by the scheme:

$$2R_3SiX + 2Na \rightarrow R_3SiSiR_3 + 2NaX\ (X = Cl, Br).$$

With all of the described methods for the synthesis of hexaalkyldisilanes the yields of these compounds usually fail to exceed 50-54%, and it is only in the experimentally difficult reaction of dimethylzinc with hexachlorodisilane, carried out in a sealed tube at 80° in the presence of ethyl ether [4], that a yield of hexamethyldisilane approaching 74% is achieved.

The higher hexaalkyldisilanes, with the alkyl radicals containing more than three carbon atoms, have not been known up to now, * and obviously their synthesis by existing methods should lead to low yields, since hexapropyldisilane is already obtained with greater difficulty from hexachlorodisilane than is hexaethyldisilane, and its yield proves to be low [5].

In this study we investigated the possibility of synthesizing hexaalkyldisilanes by the method of reacting molten sodium with the recently made readily available trialkyliodosilanes [8], in accord with the scheme

$$2R_3SiI + 2Na \rightarrow 2NaI + R_3SiSiR_3.$$

* In contrast, the hexaaryldisilanes have been described quite fully in the literature.

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In addition, we attempted to replace the sodium in this reaction by other metals, phosphorus and sulfur.

Up to now the reaction of trialkylhalosilanes with metallic sodium has been realized only on the single example of synthesizing hexaethyldisilane, which was obtained in identical yield (54%) from either the triethylbromosilane [6] or the triethylchlorosilane [7].

We hoped that the use of the trialkyliodosilanes, being much more reactive than the corresponding chlorides and bromides, would lead to considerably higher yields of the hexaalkyldisilanes, and also make it possible to easily obtain the higher members of this series.

Our attempts to cleave iodine from the trialkyliodosilane by heating the latter with a number of metals, sulfur or phosphorus, proved unsuccessful. Thus, for example, in contrast to the iodosilane H_3SiI [9], the triethyliodosilane remained completely unchanged under prolonged boiling with either sulfur or phosphorus. Also, complete failure to react was observed when the triethyliodosilane was heated with either aluminum, magnesium, zinc, mercury or copper in nitrogen-filled sealed ampoules at 140-150° for 40 hours.

At the same time, in accord with the data of Eaborn [10], we found that the triethyliodosilane reacts with magnesium in absolute diethyl ether medium to form some sort of organomagnesium compound. A study of this reaction revealed that it leads to the formation of ethylmagnesium iodide, since the triethyliodosilane, under heating, and slowly even in the cold, easily cleaves the ether into ethyl iodide and hexaethyldisiloxane (74% yield) by the scheme:

$$(C_2H_5)_3SiI + (C_2H_5)_2O \rightarrow (C_2H_5)_3SiOC_2H_5 + C_2H_5I;$$

$$(C_2H_5)_3SiOC_2H_5 + (C_2H_5)_3SiI \rightarrow (C_2H_5)_3Si{-}O{-}Si(C_2H_5)_3 + C_2H_5I.$$

Since the main reaction product of the triethyliodosilane with diethyl ether proved to be hexaethyldisiloxane, and not triethylethoxysilane, then it could be assumed that the latter reacts with the triethyliodosilane in ether medium more easily than does the ether itself. Actually, a study of the reaction of triethyliodosilane with triethylethoxysilane revealed that they easily react by the scheme given above, forming hexaethyldisiloxane and ethyl iodide (both in 91% yield). These results led us to the discovery of a general reaction for the cleavage of alkoxysilanes (and also of ethers) by iodosilanes, leading to the formation of alkyl iodides and the corresponding siloxanes, in accord with the scheme:

$$>Si{-}OR + >SiI \rightarrow RI + >Si{-}O{-}Si<$$

which was confirmed by us on a number of other examples. A similar reaction, proceeding however only in the presence of catalysts, has also been described for the chlorosilanes [12].

As a result, the opinion [10, 11] prevailing in the literature that the iodosilanes with magnesium in ether medium can give organomagnesium silicon compounds is untenable.

We further found that both the lower and higher trialkyliodosilanes react smoothly with molten sodium in the absence of solvent, forming here the corresponding hexaalkyldisilanes in 70-80% yield. In this connection the higher trialkyliodosilanes show slower reaction with sodium than do the lower members (see table). The yields of the hexamethyl- and hexaethyldisilane (78-80%) are considerably higher than by the earlier used methods for their preparation. In particular, the yield of hexaethyldisilane is 25% greater than in its synthesis from either the triethylbromo- or triethylchlorosilane [6, 7]. When we reacted tri-n-butylchlorosilane with molten sodium the yield of hexa-n-butyldisilane (47%) was 17% less than in its synthesis from tri-n-butyliodosilane (64%).

Consequently, our studied reaction of trialkyliodosilanes with molten sodium is a convenient general method for the preparation of hexaalkyldisilanes, which is based on readily available reagents and is characterized by high yields of the final products.

Hexaalkyldisilanes R_3SiSiR_3

R	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	$n_F^{20} - n_C^{20}$	Content of Si (in %) Found	Calculated	Duration of reaction (in hours)	Yield of impure product (%)	Boiling point of impure product
CH_3*	113.3° (m.p. 12.2°)	760	0.7268	1.4229	0.0092	38.13, 38.60	38.38	5	77.5	108—113°
C_2H_5**	251.7	760	0.8351	1.4790	0.0104	24.31, 24.17	24.37	5	79.6	119—120 (7 mm)
n-C_3H_7***	128.5—129	1.5	0.8291	1.4721	0.0103	17.26, 17.68	17.86	5	68.3	287—293
n-C_4H_9	187.5—188.5	1.5	0.8306	1.4694	0.0100	14.45, 14.44	14.08	10	64.2	186—190 (1.5 mm)
iso-C_5H_{11}	185.9—186	2	0.8260	1.4667	0.0094	11.95, 11.31	11.63	20	74.1	186—187 (2 mm)
n-C_6H_{13}	235—236	0.5	0.8366	1.4691	0.0092	9.55, 9.43	9.90	25	42	235—236 (0.5 mm)

* Literature data [17]: b.p. 113.0° (760 mm), d_4^{20} 0.7272, n_D^{20} 1.4229.
** Literature data [7]: b.p. 248-250° (735 mm), 87-89° (2.5 mm), d_4^{20} 0.8300, n_D^{20} 1.4759.
*** Literature data [5]: b.p. 114° (3 mm), d_4^{20} 0.8093, n_D^{20} 1.4740.

As a result of the present study we synthesized six hexaalkyldisilanes, three of them being previously unknown. The duration of reaction, the yields of the obtained hexaalkyldisilanes, their analysis data, and their physical properties are all given in the table.

All of the hexaalkyldisilanes synthesized by us are colorless viscous liquids with characteristic odor. It is interesting to mention, in contrast to the hexaaryldisilanes [13], that the hexaalkyldisilanes fail to evolve hydrogen even when boiled with either water or alcoholic caustic, or with aqueous organic bases. Also, they fail to dissolve in concentrated sulfuric acid and are not decomposed by it, which fact can be used to separate the hexaalkyldisilanes from hexaalkyldisiloxane impurities.

EXPERIMENTAL

Starting reagents. The trialkyliodosilanes were prepared either by the reaction of hexaalkyldisiloxanes with iodine and aluminum or else by the action of iodine on trialkylsilanes.

Tributylchlorosilane was prepared by the reaction of hexabutyldisiloxane with aluminum chloride [8] and had b. p. 242-243° (750 mm), d_4^{20} 0.8793, n_D^{20} 1.4471.

Triethylethoxysilane was prepared by the reaction of triethylsilane with absolute ethyl alcohol [14] and had b. p. 154.0° (760 mm), d_4^{20} 0.8160, n_D^{20} 1.4140.

Commercially pure metallic sodium, magnesium, aluminum, mercury, copper, zinc and also iodine, sulfur and red phosphorus were used.

Petroleum ether with b. p. 50-80° was purified by prolonged mechanical shaking with a mixture of sulfuric acid and oleum and after washing and drying was distilled over metallic potassium.

Special attention was given to the purification of nitrogen from traces of moisture and admixed oxygen which would cause the formation of undesirable side products – hexaalkyldisiloxanes. For this purpose cylinder nitrogen (97% N_2) was freed of oxygen by passage through a saturated solution of NH_4Cl in NH_4OH in the presence of copper thread [15] after which it was passed through absorbers with 50% H_2SO_4, solid KOH, conc. H_2SO_4, P_2O_5, a column filled with sodium wire and finally, through a test tube with fused sodium.

Analytical method. All the reactions of trialkyliodosilanes (and also of tributylchlorosilane) with sodium were carried out in a thick-walled round-bottomed 250 ml 3-necked flask fitted with reflux condenser, high-speed mechanical stirrer with mercury seal, dropping funnel and nitrogen inlet. The reflux condenser was connected to a Tishchenko bottle with concentrated sulfuric acid.

Into the nitrogen-filled reaction flask was placed metallic sodium (molar ratio Na : R_3SiX = 2), and the flask was then heated on a polysiloxane bath to 130-140°. The corresponding trialkyliodosilane was introduced drop-wise in the course of 30-45 minutes with energetic stirring into the fused sodium and the flask was further heated at the cited temperature for 5-25 hours (depending on the structure of the initial trialkyliodosilane). All syntheses were carried out in a stream of pure dry nitrogen (rate of 4-5 bubbles per minute).

When the reaction was complete, the hexaalkyldisilane was extracted from the reaction mixture with four 80-100 ml portions of petroleum ether. The precipitate of metallic sodium and sodium iodide was filtered off in a nitrogen atmosphere, washed with petroleum ether and was rapidly dissipated. After petroleum ether was driven off from the combined filtrate, the remaining hexaalkyldisilane was distilled over metallic sodium or potassium in a column with an efficiency of 12 theoretical plates (the higher hexaalkyldisilanes were distilled in vacuum).

The method for determination of the physical constants and the accuracy of their determination was previously described [16]. For determination of constants, all the substances were given a repeated distillation in the column and the intermediate portions of the constant boiling fractions were taken off.

Determination of silicon in the hexaalkyldisilanes was carried out by the method of wet combustion with a mixture of fuming nitric acid and oleum. As an example we present a description of the synthesis of hexa-n-butyldisilane.

Synthesis of hexa-n-butyldisilane. a) 65.3 g (0.2 mole) of tri-n-butyliodosilane was added drop-wise in the course of 45 minutes with vigorous stirring to 9.66 g (0.42 mole) of fused sodium and the mixture was then heated and stirred at 130-140° for 10 more hours. Fractional distillation of the reaction products separated by extraction yielded 25.6 g hexa-n-butyldisilane with b. p. 185.5-190° (1.5 mm), i.e., 64.2%. When the above reaction was carried out for 5 hours the yield of hexa-n-butyldisilane was 15.8 g (39.6%).

b) 47.0 g (0.2 mole) tri-n-butylchlorosilane was added drop-wise in the course of 30 minutes with vigorous stirring to 9.66 g (0.42 mole) fused sodium. After this, the mixture was heated and stirred at 130-140° for 35 hours. The yield of hexa-n-butyldisilane, isolated the usual way, b. p. 187-193° (1.6 mm), was 18.6 g (46.6%).

Reaction of triethyliodosilane with magnesium, aluminum, copper, zinc, mercury. 12.1 g (0.05 mole) of triethyliodosilane and 0.2 mole powder of one of above metals were heated in a sealed ampoule, filled with dry pure nitrogen at 140-150° for 40 hours. Distiilation of the contents of the ampoule showed that in all cases triethyliodosilane remained completely unchanged.

Reaction of triethyliodosilane with sulfur and phosphorus. A mixture of 24.2 g (0.1 mole) triethyliodosilane was boiled in a nitrogen atmosphere for 24 hours with 0.2 mole sulfur powder or with red phosphorus. In both cases distillation of the reaction mixture yielded unchanged triethyliodosilane.

Reaction of triethyliodosilane with diethyl ether. A solution of 12.1 g (0.05 mole) triethyliodosilane in 22.2 g (0.3 mole) absolute diethyl ether was boiled in a nitrogen atmosphere in a round-bottomed flask fitted with a reflux condenser. Distillation of the reaction mixture yielded 4.5 g (74.8%) hexaethyldisiloxane with b. p. 225-235°, n_D^{20} 1.4339. The lower-boiling fraction with b. p. 34-72° which consisted of ether and ethyl iodide reacted with magnesium to form C_2H_5MgI which gave off ethane when water was added.

Reaction of triethyliodosilane with triethylethoxysilane. 18.2 g (0.075 mole) triethyliodosilane and 12.0 g (0.075 mole) triethylethoxysilane were heated to a slight boil in the course of 20 hours in a 50 ml distilling flask fitted with a 20 cm Vigreux column; 10.6 g (91%) ethyl iodide with b. p. 72-73° was driven off. Distillation of the residue yielded 15.9 g (91%) hexaethyldisiloxane with b. p. 230-238°, n_D^{20} 1.4341.

SUMMARY

A method was developed for the synthesis of hexaalkyldisilanes via the reaction of trialkyliodosilanes with molten sodium. With this method six hexaalkyldisilanes were synthesized in yields up to 80%, three of which were previously unknown. It was shown that triethyliodosilane reacts with diethyl ether and with triethylethoxysilane, forming hexaethyldisiloxane in both cases.

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* T. p. = C. B. Translation pagination.

SYNTHESIS OF p-DIVINYLBENZENE

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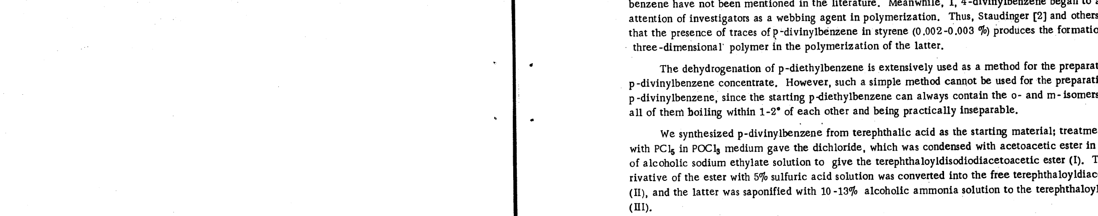
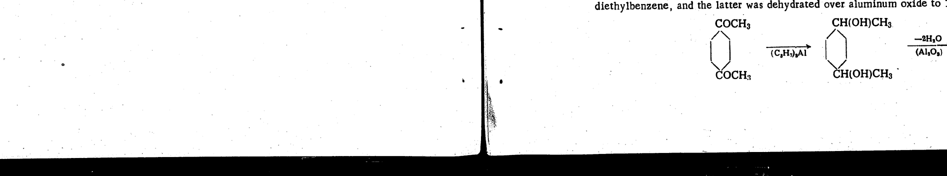
p-Divinylbenzene was first synthesized by Ingle in 1894 [1] by the vacuum-distillation of 1', 4'-dibromo-1, 4-diethylbenzene with quinoline, the former in turn obtained by the sodium amalgam reduction of 1, 4-diacetylbenzene, with subsequent treatment of the intermediate 1', 4'-dihydroxy-1, 4-diethylbenzene with hydrogen bromide (at 0° in acetic acid medium). Since then other methods for the synthesis of pure p-divinylbenzene have not been mentioned in the literature. Meanwhile, 1, 4-divinylbenzene began to attract the attention of investigators as a webbing agent in polymerization. Thus, Staudinger [2] and others [3] mention that the presence of traces of p-divinylbenzene in styrene (0.002-0.003 %) produces the formation of a three-dimensional polymer in the polymerization of the latter.

The dehydrogenation of p-diethylbenzene is extensively used as a method for the preparation of a technical p-divinylbenzene concentrate. However, such a simple method cannot be used for the preparation of pure p-divinylbenzene, since the starting p-diethylbenzene can always contain the o- and m-isomers as impurities, all of them boiling within 1-2° of each other and being practically inseparable.

We synthesized p-divinylbenzene from terephthalic acid as the starting material; treatment of the acid with PCl_5 in $POCl_3$ medium gave the dichloride, which was condensed with acetoacetic ester in the presence of alcoholic sodium ethylate solution to give the terephthaloyldisodiodiacetoacetic ester (I). The sodio derivative of the ester with 5% sulfuric acid solution was converted into the free terephthaloyldiacetoacetic ester (II), and the latter was saponified with 10-13% alcoholic ammonia solution to the terephthaloyldiacetic ester (III).



The terephthaloyldiacetic ester obtained in this manner was then saponified with 10% sulfuric acid to p-diacetylbenzene; the p-diacetylbenzene was reduced with aluminum isopropoxide to 1', 4'-dihydroxy-1, 4-diethylbenzene, and the latter was dehydrated over aluminum oxide to 1, 4-divinylbenzene:



The scheme shown here for the synthesis of p-divinylbenzene, including the step of obtaining the p-diacetylbenzene, represents the synthesis of the latter by the Berend and Herms method [4]. However, we came to make some changes and improvements in the operation of the process. The synthesis was run by a different method for the step p-diacetylbenzene $\longrightarrow$ p-divinylbenzene. Thus, instead of using sodium amalgam for the reduction of 1, 4-diacetylbenzene we used aluminum isopropoxide [5], and further, instead of the processes used by Ingle of hydrobromination and subsequent dehydrobromination of the intermediate products, we used the method of the catalytic dehydration of 1', 4'-dihydroxy-1, 4-diethylbenzene, in that way simplifying somewhat the complicated scheme for the synthesis of p-divinylbenzene.

EXPERIMENTAL

Synthesis of terephthaloyldiacetoacetic ester. 52 g acetoacetic ester was placed in a 3-necked flask and through side tubes was slowly introduced sodium ethylate (18.4 g Na in 320 ml anhydrous alcohol) and a solution of 46.6 g terephthalyl dichloride * in 800 ml absolute ether with continual mixing and cooling. The reaction mixture was then held for 18 hours at 0°.

The yellow crystalline precipitate which formed upon standing was filtered off and dried. The dried product was then mixed with ice water to which 5% sulfuric acid was slowly added with mixing until the reaction mass changed from yellow to milk-white.

The free terephthaloyldiacetoacetic ester was isolated at first in the form of curds which after standing for 3-4 hours became crystalline in structure. After washing and drying, the product was recrystallized from alcohol. M. p. 101-102°. Yield 70%.

Saponification of terephthaloyldiacetoacetic ester to terephthaloyldiacetic ester. In a round-bottomed flask was placed 40 g terephthaloyldiacetoacetic ester and 200 ml 10% alcoholic solution of ammonia. The reaction mixture was heated for 1 hour to 60°, then cooled and kept for 18 hours in a refrigerator. The precipitate which came down upon standing was filtered off and treated three times with ether. The total ethereal extract was washed with water. After the ether was driven off, the product recrystallized from alcohol. M. p. 69-70°. Yield 65%.

Hydrolysis of terephthaloyldiacetic ester in p-diacetylbenzene. 15 g terephthaloyldiacetic ester and 150 ml 10% sulfuric acid were placed in a round-bottomed flask fitted with mechanical stirrer. The mixture was heated with reflux condenser on a glycerin bath at 101-102° for 7-8 hours until the evolution of CO_2 ceased. After hydrolysis, the still hot solution was rapidly filtered and then the filter was washed with 3% aqueous solution of NaOH (100-200 ml). Upon cooling, white acicular crystals came down from the filtrate which after drying, had m. p. 114-114.5°. The yellowish residue on the filter was dried and recrystallized from hot alcohol and crystals were obtained with m. p. 113-114°.

The total yield of product reached 74%.

Reduction of 1, 4-diacetylbenzene to 1', 4'-dihydroxy-1, 4-diethylbenzene. In a round-bottomed flask was placed 75 g 1, 4-diacetylbenzene and a solution of aluminum isopropoxide in isopropyl alcohol (9 g Al in 300 ml isopropyl alcohol).

The reaction mixture was heated until the acetone was driven off and then treated with ice and water, acidified with hydrochloric acid. The product was extracted with ether which was driven off in the cold

* Prepared from terephthalic acid and PCl_5 in a yield of 86-87%.

under the slight vacuum of a water-jet pump. The crude product thus obtained was an orange oil with a distinct odor and, according to Fairley, contained 70% 2', 4'-dihydroxy-1, 4-diethylbenzene. The crude product could not be purified since at 115-116° (4 mm) the substance almost completely resinified.

Preparation of p-divinylbenzene. 25 g of crude 1', 4'-dihydroxy-1, 4-diethylbenzene was passed for 30 minutes from a biuret into a quartz tube (800 mm long, internal diameter 11 mm), filled with 25 g of finely granulated aluminum oxide.

The dehydration process was carried out at a tube furnace temperature of 280-300°. 3 g of white crystalline product was obtained which (after prolonged drying over $CaCl_2$), according to Kaufman, contained 99.3% 1, 4-divinylbenzene. Yield about 22%. M. p. 30°.

Found %: C 92.12, 92.06; H 7.87, 7.9. $C_{10}H_{10}$. Calculated %: C 92.31; H 7.69.

SUMMARY

A method was described for the synthesis of p-divinylbenzene from terephthalic acid via its transition into p-diacetylbenzene, followed by the reduction of the latter with aluminum isopropoxide to 1', 4'-dihydroxy-1, 4-diethylbenzene and the dehydration of this diol over aluminum oxide.

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SELECTIVE DEHALOGENATION OF DICHLOROACRIDINES WITH THE AID OF SKELETAL NICKEL

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Catalytic reductive dehalogenation in the presence of skeletal nickel has been insufficiently studied. According to literature data, it does not seem possible to evaluate the ability of skeletal nickel for selective dehalogenation even in compounds containing two halogen atoms that differ sharply in their mobility. Nevertheless, the removal of the more labile halogen atom of the two present in a compound is of practical interest.

The subjects that seemed of interest to us for selective dehalogenation via catalytic hydrogenation were a number of dichloroacridines.

As is known [1, 2], a halogen in the 9 position of acridine is extremely labile. This permitted us to consider the possibility of selectively removing the halogen in the 9 position from, for example, the 3, 9-dichloroacridine molecule.

It is asserted in the literature that the preparation of 3-chloroacridine by the reductive dehalogenation of 3, 9-dichloroacridine cannot be realized with the aid of skeletal nickel, since it appears as though both of the halogen atoms are cleaved simultaneously.

Recently, a new method was proposed for the dehalogenation of substituted 9-chloroacridines. With this method the substituted 9-chloroacridine is reacted with p-toluene-sulfanilylhydrazine in chloroform; heating of the addition product with dilute alkali gives the corresponding substituted acridine in good yield [3].

As the result of our reductive dehalogenation of 3, 9-dichloroacridine in the presence of skeletal nickel, taken in a 1 : 1 ratio, and 1 equivalent of potassium hydroxide, with introduction of hydrogen from without, in alcohol medium, we were able to obtain 3-chloro-9, 10-dihydroacridine as the main reaction product.

The secondary product isolated from the reaction mixture was 3, 3'-dichlorobiacridyl.

To prove the position of the halogen atom in the chloroacridine obtained by us, we converted it into the chloroacridone by oxidation with sodium dichromate under heating in glacial acetic acid *.

* The preparation of the 9-acridone in good yield by the direct oxidation of the acridine has not been successful [6].

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Treatment of the chloroacridone with phosphorus oxychloride gave the starting 3, 9-dichloroacridine.

The selective dehalogenation of 2-methoxy-6, 9-dichloroacridine was realized by us under the same conditions, using 1 equivalent of potassium hydroxide, the same as in the dehalogenation of the 3, 9-dichloroacridine. Here the main reaction product was 2-methoxy-6-chloro-9, 10-dihydroacridine, obtained in 41% yield.

The oxidation of 2-methoxy-6-chloro-9, 10-dihydroacridine with ferric chloride in dilute hydrochloric acid gave us 2-methoxy-6-chloroacridine in 53.6% yield. In the presence of 2 equivalents of potassium hydroxide the main reaction product was 2-methoxy-9, 10-dihydroacridine, isolated in 81% yield. Here the formation of the dimethoxydichlorobiacridyl was not revealed.

The oxidation of 2-methoxy-9, 10-dihydroacridine with ferric chloride in dilute hydrochloric acid gave 2-methoxyacridine.

EXPERIMENTAL

3-Chloro-9, 10-dihydroacridine. 1.86 g 3, 9-dichloroacridine (m. p. 166-167°) [8] was dissolved with heating in 600 ml methanol. Upon cooling, 0.42 g KOH and 1.85 g nickel slurry were added to the solution. The mixture was hydrogenated in a hydrogenation bottle while being mixed in a shaker; hydrogenation lasted 45 minutes.

The reaction mixture was filtered and the catalyst was washed with methanol. Upon standing, pale cream-colored needles (from filtrate) came down and were filtered off, washed with water, dried and weighed 0.07 g. The substance was dissolved in 4 ml pyridine with boiling, the solution was treated with charcoal, filtered; the filtrate was diluted with a two-fold volume of water; the precipitate which came down was filtered off, washed with water and dried. Yield 0.06 g of substance, m. p. 355-357°; its mixed sample with known 3, 3'-dichloro-9, 9'-biacridyl [4] melted without depression. Methanol was driven off from the alcoholic filtrate until 25 ml volume remained, the precipitate which came down was filtered off, washed with methanol and then with water. Reprecipitation of this precipitate from pyridine yielded a further 0.08 g of 3, 3'-dichloro-9,9'-biacridyl.

After separation of the dichlorobiacridyl, the filtrate was diluted with water, the precipitate which came down (yellowish lustrous leaflets) was filtered off, washed with water, dried and then again dissolved in methanol; the solution was treated with charcoal, filtered, the filtrate was diluted with a two-fold volume of water. The precipitate which came down was filtered off, washed with water, dried ; weight 1.37 g, m. p. 110-113°. The obtained substance was treated with 5% hydrochloric acid, the undissolved residue was washed with water and then recrystallized from aqueous 50% methanol. The obtained yellowish lustrous leaflets had m. p. 117-118°; weight 1.06 g (66.4%).

Found %: C 72.54; H 4.47. $C_{13}H_{10}NCl$. Calculated %: C 72.39; H 4.62.

The substance was soluble in the cold in benzene, acetone, methanol, ether,and insoluble in water and in 2 N hydrochloric acid.

3-Chloroacridine. A solution of sulfuric acid, consisting of 300 ml water and 3.88 g chemically pure sulfuric acid was heated to the boil and to this was added 3 g of 3-chloro-9, 10-dihydroacridine and then in two portions, within 5 minutes, a solution of 1.8 g potassium chromate in 25 ml water. The reaction solution was boiled for 10 minutes. A solution of 4.8 g potassium chromate in 30 ml water, heated to the boil, was then added to the reaction solution. The mixture was boiled for 5 minutes and then set aside until the following day.

The orange-yellow precipitate which came down from solution was separated by filtration, placed in 75 ml hot water and treated upon heating with concentrated ammonia (16 ml). The precipitate of the substance was filtered off, washed with water and treated with 5% hydrochloric acid (40 ml). The resulting solution was filtered free of traces of chloroacridine; after cooling, the filtrate was precipitated with dilute ammonia. The substance which came down was washed with water and dried; weight 2.57 g. After recrystallization from 50% aqueous methanol, the substance was obtained in the form of long, slender colorless needles, m. p. 132-133°; weight 2.49 g (70%).

Found %: C 72.86; H 4.02; Cl 16.78. $C_{13}H_8NCl$. Calculated %: C 73.07; H 3.77; Cl 16.59.

3-Chloroacridine was readily soluble in methanol, ether, benzene, acetone and insoluble in water.

3-Chloroacridine hydrochloride crystallized from dilute hydrochloric acid in the form of slender yellow needles, m. p. 248-249° with decomposition. The hydrochloride was readily soluble in water, methanol,and insoluble in ether, acetone and in benzene. From methanolic solution it was precipitated with ether in the form of yellow needles.

3-Chloroacridone. 0.8 g of 3-chloroacridine was dissolved in 5 ml glacial acetic acid and to this was added a solution of 0.67 g sodium bichromate in 5 ml glacial acetic acid. The solution was heated at the boil for 4.5 hours. After cooling, the precipitate which came down was filtered off and washed with water; yield 0.1 g of substance with m. p. above 360°. The filtrate was run into cold water, the precipitate was filtered off, washed with water and dried at 110°. The total yield was 0.4 g of substance with m. p. above 360°, corresponding in properties to 3-chloroacridone [7]. When the substance was reacted with phosphorus oxychloride, the usual treatment [8] yielded yellow needles, m. p. 166-167°, identical to known 3, 9-dichloroacridine.

2-Methoxy-6-chloro-9, 10-dihydroacridine. A hot solution of 1.3 g 2-methoxy-6, 9-dichloroacridine (m. p. 162-163° [9]) in 350 ml methanol was placed in a reaction bottle for hydrogenation. When the solution was cooled to room temperature, a yellow flocculent precipitate of methoxydichloroacridine partially came down. 0.26 g KOH (1 equiv.), dissolved in 50 ml methanol and 1.3 g nickel slurry were then added to the reaction bottle. The mixture was hydrogenated as usual with mixing on a shaker. After absorption of 270 ml hydrogen, reduction was stopped. The catalyst precipitate was filtered off, washed with hot methanol and then treated with pyridine at the boil; substituted biacridyl was not detected at this point.

After driving off the methanol from the filtrate in vacuum at room temperature, the 25 ml of liquid residue and the precipitate which came down were placed on a filter; the precipitate was washed with water, methanol and dried; weight 0.45 g. After 2-fold recrystallization from benzene, 2-methoxy-6-chloro-9, 10-dihydroacridine was obtained in the form of yellow needles, m. p. 185-186° [10].

Found %: N 5.51; Cl 14.30. $C_{14}H_{12}ONCl$. Calculated %: N 5.70; Cl 14.43.

2-Methoxy-6-chloroacridine. A solution of 1.5 g ferric chloride in 18 ml 5% hydrochloric acid was added to a suspension of 0.7 g 2-methoxy-6-chloro-9, 10-dihydroacridine in 22 ml 5% hydrochloric acid. The mixture was slowly heated with mixing to the boil, after which the solution was filtered while hot. Upon cooling, the hydrochloride salt of the substance came down. This salt was filtered off, washed with 3% hydrochloric acid, dissolved in 15 ml water and upon mild heating, the solution was treated with dilute ammonia. The colorless precipitate which came down was filtered off, washed with water and dried, weight 0.37 g. The substance was recrystallized from methanol with charcoal. 2-Methoxy-6-chloroacridine was obtained in the form of lemon-yellow needles, m. p. 174-175°.

Found %: Cl 14.41; N 5.60. $C_{14}H_{10}ONCl$. Calculated %: Cl 14.54; N 5.74.

2-Methoxy-6-chloroacridine was soluble in methanol, acetone, ether, benzene,and insoluble in water. In concentrated sulfuric acid it gave a yellow solution with green fluorescence. 2-Methoxy-6-chloroacridine hydrochloride was obtained in the form of yellow needles, m. p. 251-252°; it is soluble in water and in methanol, insoluble in ether, benzene and in acetone.

2-Methoxy-9, 10-dihydroacridine. 1.39 g of 2-methoxy-6, 9-dichloroacridine was dissolved in 350 ml methanol with heating. The solution was cooled to room temperature and then a solution of 0.56 g KOH in 20 ml methanol and 1.4 g nickel slurry, suspended in 30 ml methanol was added. The mixture was hydrogenated as usual until absorption of hydrogen stopped.

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The reaction mixture was filtered, the separated catalyst was washed with hot methanol, after which it was treated with pyridine at the boil. Upon dilution of the pyridine with water, a precipitate of the substituted biacridyl was not detected.

Methanol was driven off from the alcoholic filtrate and the residue was diluted with water. The white substance which came down was filtered off, washed with water and dried; weight 0.85 g, m. p. 120-121°. The substance was recrystallized from methanol, (1 : 15); white flakes were obtained which melted at 139.5-140.5°; for 2-methoxy-9, 10-dihydroacridine, m. p. 139.5-140.5° is given [11].

2-Methoxyacridine. 0.85 g of methoxyacridine, obtained as described above, was suspended in 30 ml 5% hydrochloric acid, to which was then added a solution of 1.4 g ferric chloride in 18 ml 5% hydrochloric acid. The mixture was slowly heated to the boil. After complete solution of the precipitate, the solution was filtered while hot. Upon cooling, the hydrochloride salt of the substance came down from the filtrate. The salt was filtered off and washed with 3% hydrochloric acid in which it was practically insoluble. The hydrochloride was dissolved in a small volume of water with mild heating and to this solution was added dilute ammonia; the base separated out in the form of oil which solidified upon cooling. The base was separated, dissolved in methanol, the solution was heated with charcoal at the boil and filtered. Upon cooling, yellow needles came down from the filtrate. The crystals which came down were separated, washed with water and dried; weight 0.37 g, m. p. 102-103°. After recrystallization from methanol, the substance was obtained in the form of yellow needles, m. p. 103-104°.

Found %: N 6.86. $C_{14}H_{11}ON$. Calculated %: N 6.69.

The properties of the obtained substance corresponded to those described for 2-methoxyacridine [11].

SUMMARY

1. Observations on the dehalogenation of some dichloroacridines revealed, when two halogen atoms showing unequal mobility are present in the molecule, that the more labile halogen atom in the 9 position can be removed via catalytic reductive dehalogenation in presence of skeletal nickel; here the necessary condition for selective halogen removal is the use of only one equivalent of alkali.

2. It was shown that 3-chloroacridine can be obtained by the reductive dehalogenation of 3, 9-dichloroacridine in the presence of skeletal nickel.

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DIRECT SYNTHESIS OF ARYL β-CHLOROVINYL KETONES

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β-Chlorovinyl ketones show high reactivity due to the presence of a carbonyl group, an active double bond and a labile chlorine atom in their molecule. In previous investigations we developed, based on β-chlorovinyl ketones, a number of new methods for the synthesis of aliphatic, alicyclic and heterocyclic compounds [1]. However, at the present time only the simplest aliphatic β-chlorovinyl ketones of type Alk $-CO-CH=CHCl$, can be considered as being extensively available representatives of this class of compounds, the synthesis of which was developed in detail [2] and consists of condensing fatty acid chlorides with acetylene in the presence of aluminum chloride:

$$\mathrm{AlkCOCl + CH{\equiv}CH \xrightarrow{AlCl_3} AlkCOCH{=}CHCl.}$$

In contrast to the aliphatic β-chlorovinyl ketones, their aromatic analogs $ArCOCH=CHCl$ are considerably less available. The synthesis of the latter was recently developed [3] by the scheme:

$$\mathrm{ArCOCH_3 + HCO_2C_2H_5 \xrightarrow{Na} ArCOCH{=}CHONa \xrightarrow{SOCl_2} ArCOCH{=}CHCl.}$$

The use of this reaction is limited by the poor availability of substituted acetophenones and the laborious nature of the method.

In this paper we communicate on the direct synthesis of aryl β-chlorovinyl ketones, analogous to the synthesis of their aliphatic analogs, by the scheme:

$$\mathrm{ArCOCl + CH{\equiv}CH \xrightarrow{AlCl_3} ArCOCH{=}CHCl.}$$

It is stated in the patent literature [4] that the condensation of benzoyl chloride with vinyl chloride yields phenyl β-chlorovinyl ketone; however, these data are not confirmed by later studies [5]. A more detailed study of this reaction revealed that phenyl β, β-dichloroethyl ketone is formed here, which is converted into the corresponding β-chlorovinyl ketone only after additional treatment [6].

The direct synthesis of aryl β-chlorovinyl ketones from the chlorides of aromatic acids and acetylene is of considerable interest, since it makes this type of compound also widely available. The condensation of benzoyl chloride with acetylene in the presence of aluminum chloride under the conditions used for the preparation of aliphatic β-chlorovinyl ketones [2], in carbon tetrachloride medium at 0-10°, failed to give the desired result – the acid chloride proved unreactive under these conditions and was recovered unchanged. This result can be explained by the lower activity shown by the chlorine atom of aromatic acid chlorides when compared with their aliphatic analogs. Taking into consideration the relatively great stability of aryl β-chlorovinyl ketones [3], we investigated more drastic conditions for the reaction of benzoyl chloride with acetylene. The best results were obtained when acetylene was passed into a solution of the benzoyl chloride complex with aluminum chloride. The complex was prepared in advance at a temperature not exceeding 10° in dichloroethane solution. The use of this solvent gave better results than did the use of carbon tetrachloride. The saturation with acetylene was run at 40-50° for a period of 6-7 hours. Despite the fact that here a small portion of the acid chloride fails to react, still such a method of operation is more satisfactory than when more complete utilization of the acid chloride is made (passage of acetylene for more than 10 hours), since in the latter case the strong tarring of the reaction mixture makes it difficult to isolate the reaction product. The yields of phenyl β-chlorovinyl ketone reached 65-70%, based on reacted acid chloride.

This method was extended to the preparation of aryl β-chlorovinyl ketones with substituents in the aromatic nucleus. By reacting the corresponding acid chlorides we obtained p-tolyl β-chlorovinyl ketone, p-chlorophenyl β-chlorovinyl ketone, o-bromophenyl β-chlorovinyl ketone and p-nitrophenyl β-chlorovinyl ketone. It is also more convenient in these cases to run the reaction under acetylene passage for 6-8 hours (at 40-50°).

The unreacted acid chloride is easily removed by simple distillation. The yields of substituted aryl β-chlorovinyl ketones, based on reacted acid chloride, constitute 55-70%, and based on acid chloride taken – 50-60%. The isolation of the aryl β-chlorovinyl ketones is usually achieved by vacuum-distillation. Only the p-nitrophenyl β-chlorovinyl ketone is an exception; its distillation is associated with the danger of explosion, which occurred in our work. We used a different method for its isolation. The aryl β-chlorovinyl ketones obtained by us are relatively stable compounds, which can be kept for some time without change. p-Chlorophenyl β-chlorovinyl ketone, o-bromophenyl β-chlorovinyl ketone and p-nitrophenyl β-chlorovinyl ketone, obtained by us for the first time, are crystalline substances. The last of the mentioned compounds cannot be obtained by the earlier described method [3], since the presence of the nitro group excludes the possibility of formylation. This emphasizes again the fact that our developed method possesses more general value than does the earlier method.

Consequently, the condensation of acid chlorides with acetylene in the presence of aluminum chloride can be realized in both the aliphatic and aromatic series.

EXPERIMENTAL

Phenyl-β-chlorovinyl ketone. A solution of 100 g benzoyl chloride in 250 ml dichloroethane was placed in a 500 ml 3-necked flask fitted with stirrer, reflux condenser, acetylene lead tube extending to the bottom of the flask and thermometer. The solution was cooled to 0° and 95 g of anhydrous aluminum chloride was added with mixing and cooling at such a rate that the temperature of the mixture did not rise above 10°. When all the aluminum chloride had been added, through the reaction mixture with vigorous stirring was passed acetylene for 6-7 hours, the temperature of the reaction mixture being kept at about 40-50°. The reaction mixture was then decomposed upon being poured on ice; the dichloroethane layer was separated, the aqueous layer was twice extracted with chloroform, the extracts were combined with the main portion of substance and dried over calcium chloride and potash. The solvent was driven off and the residue was vacuum-distilled. At 52-54° (2 mm) 15-18 g of initial benzoyl chloride distilled over and then after a small intermediate fraction phenyl-β-chlorovinyl ketone was collected, b. p. 92-96° (2 mm); yield 70-75 g (65-70%, calculated on reacted benzoyl chloride). After a second distillation, phenyl-β-chlorovinyl ketone had b. p. 80-82° (0.5 mm), 85-87° (1 mm).

n_D^{20} 1.5860, d_4^{20} 1.2062. Literature data: b. p. 118-120° (10 mm) [3], n_D^{20} 1.5742; b. p. 125-127° (18 mm) [5].

Found %: Cl 21.07, 21.33. C_9H_7OCl. Calculated %: Cl 21.33.

p-Tolyl-β-chlorovinyl ketone was obtained in the same manner as phenyl-β-chlorovinyl ketone from 28 g p-toluoyl chloride and 25 g aluminum chloride in 60 ml dichloroethane at 45-50°; acetylene was passed

for 6.5-7 hours. Distillation yielded 2.2-3.2 g of initial acid chloride (b. p. 90-100° at 5 mm) and 23.0 g p-tolyl-β-chlorovinyl ketone, b. p. 123-127° (5 mm); yield 70-75%, based on the reacted acid chloride. After a second distillation, p-tolyl-β-chlorovinyl ketone had b. p. 114-116° (2 mm).

n_D^{20} 1.5835, d_4^{20} 1.1693. Literature data: [3]; b. p. 118-120° (5 mm) n_D^{20} 1.5826, d_4^{20} 1680.

p-Chlorophenyl-β-chlorovinyl ketone was prepared from 30 g p-chlorobenzoyl chloride and 22.6 g aluminum chloride in 60 ml dichloroethane at 30-40°; acetylene was passed for 6.5-7 hours. Distillation yielded 6.0-7.3 g p-chlorobenzoyl chloride (b. p. 70-80° at 3 mm) and 19.0-20.4 g p-chlorophenyl-β-chlorovinyl ketone (b. p. 114-116° at 2 mm), which completely crystallized in the receiver. After recrystallization from petroleum ether (40-70°), p-chlorophenyl-β-chlorovinyl ketone was in the form of colorless needles with m. p. 35.5-36.5°. It was readily soluble in ordinary organic solvents and less soluble in petroleum ether, insoluble in water.

Found %: Cl 35.59, 35.52. $C_9H_6OCl_2$. Calculated %: Cl 35.27.

o-Bromophenyl-β-chlorovinyl ketone was prepared from 44 g o-bromobenzoyl chloride and 27 g aluminum chloride in 150 ml dichloroethane at 30-40°; acetylene was passed for 6.5-7 hours. Distillation yielded 28-30.5 g o-bromophenyl-β-chlorovinyl ketone (b. p. 118-122° at 1.5-2 mm), which completely crystallized in the receiver. Yield 56.5-62%, based on the acid chloride taken. After recrystallization from petroleum ether, o-bromophenyl-β-chlorovinyl ketone was in the form of colorless needles with m. p. 45.5-46.5°. It was readily soluble in ordinary organic solvents, less soluble in petroleum ether, insoluble in water.

Found %: C 44.37, 44.21; H 2.51, 2.63. C_9H_6OClBr. Calculated %: C 44.02; H 2.46.

p-Nitrophenyl-β-chlorovinyl ketone was prepared from 30 g p-nitrobenzoyl chloride and 26 g aluminum chloride in 70 ml dichloroethane (the complex was prepared at room temperature), acetylene was passed for 8.5-9 hours. After decomposition of the reaction mass, the combined extracts were boiled with an equal volume of aqueous saturated solution of sodium bicarbonate for 4-5 hours on a water bath to remove the unreacted acid chloride. The aqueous layer was separated and acidified until a definite acid reaction was obtained on Congo. The p-nitrobenzoic acid which came down was filtered off. The dichloroethane solution was dried over potash, the solvent was driven off on a water bath and toward the end – in vacuum. The residue was repeatedly extracted with a boiling mixture of petroleum ether and ethyl acetate. The resulting solution was steamed down to dryness and the residue consisted of yellow crystals of p-nitrophenyl-β-chlorovinyl ketone with m. p. 82-83°; yield 17.0-17.5 g (57.5-60.2%, based on the reacted p-nitrobenzoyl chloride). After recrystallization from petroleum ether, p-nitrophenyl-β-chlorovinyl ketone was in the form of yellow crystals with m. p. 88.5-89°. It was soluble in ordinary organic solvents, moderately soluble in ethyl acetate, less soluble in petroleum ether, insoluble in water.

Found %: C 51.36, 51.38; H 2.95, 2.98; N 6.69, 6.70. $C_9H_6O_3NCl$. Calculated %: C 51.08; H 2.86; N 6.62.

SUMMARY

A general method was developed for the synthesis of aryl β-chlorovinyl ketones via the reaction of aromatic acid chlorides with acetylene in the presence of aluminum chloride at 40-50° in dichloroethane solution (in 55-70% yield).

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OXIDATION OF CYCLOOCTATETRAENE TO TEREPHTHALIC ACID

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Reppe and coworkers described [1] the oxidation of cyclooctatetraene by means of different oxidizing agents and under various conditions. In particular, when chromic acid in glacial acetic acid was used for the oxidation they isolated two fractions: "acid", assumed to be entirely terephthalic acid, and identified through the dimethyl ester, and "neutral", in which benzaldehyde was found.

Since the preparation of terephthalic acid in general, and from cyclooctatetraene in particular, is of definite interest, we repeated these experiments. In accord with the data obtained by us (see table), the scheme proposed by Reppe for the oxidation of cyclooctatetraene with chromic anhydride should be supplemented by the formation of considerable amounts of benzoic acid remaining in the "acid" fraction together with terephthalic acid.

EXPERIMENTAL

To a solution of 5 g cyclooctatetraene in 100 ml glacial acetic acid in a 1 liter round-bottomed flask fitted with mechanical stirrer, thermometer and dropping funnel, was added a solution of chromic anhydride ($\sim 33\%$) in aqueous acetic acid (75%). Upon addition of the oxidizing agent, the temperature of the reaction mixture at first rose to 50-70° (depending on the rate of addition of the oxidizing agent) and then it fell somewhat, changing but little until all the oxidizing agent had been added. In most of the experiments, after addition of all of the oxidizing agent, stirring was continued for 30 minutes more at room temperature and in a number of experiments the temperature was held at 50-60° by heating on a water bath for 2.5 hours (see table, Experiments 9-12). After cooling, the reaction mixture was diluted with 500 ml water and extracted 4 times (150 ml portions) with ether. The combined ethereal extract was washed 2 times (400 ml portions) with water and was then treated with 100 ml of 5% caustic soda solution. The alkaline layer, separated from the ether, was heated to the boil and the "acid fraction" was precipitated by addition of a dilute solution of sulfuric acid. The ethereal extract was driven off on a water bath. The residue was crude benzaldehyde.

The content of benzoic acid in the "acid" fraction was determined by sublimation of a 0.05-0.1 g weighed sample at 180-200° for 1 hour (by difference). The sublimate and benzoic acid were proven identical by determination of the melting point of the sublimate and a mixed sample. The content of terephthalic acid was determined (by difference) through sublimation of the residue at 300-320° for 1.5 hours. That this sublimate and terephthalic acid were identical was confirmed by preparation of the dimethyl ester and determination of the melting point of the product's ester and that of a mixed sample with the dimethyl ester of a known specimen. The experimental conditions and results are given in the table.

Since the determination of the content of benzoic and terephthalic acid by the described method might not have been completely accurate due to partial decomposition of the oxidation products during sublimation and some volatilization of terephthalic acid with benzoic acid [2], the acid number [3] of the "acid fraction" samples was determined. 0.07-0.1 g of weighed acid fraction sample was dissolved in

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Oxidation of Cyclooctatetraene with Chromic Anhydride. Initial Quantity of Cyclooctatetraene 5 g; Glacial Acetic Acid 100 ml.

No.	CrO_3 (in g)	Duration of addition of CrO_3 (in min.)	Duration of reaction (in min.)	Temperature range of reaction	Quantity of "acid" fraction (in g)	Quantity of crude benzaldehyde (in g)	Composition of "acid" fraction (in %): Benzoic acid	Terephthalic acid	Residue and losses	Yield of oxidation products (in %, calculated on taken cyclooctatetraene): Benzoic acid	Terephthalic acid	Benzaldehyde
1	20	45	45	45—50	1.3	1.9	74.2	18.9	6.9	16.3	3.1	38
2	20	40	70	45	1.4	1.5	64.8	29.4	5.8	15.4	5.2	30
3	20	90	90	40—45	1.0	2.1	47.5	38.5	14.0	7.9	4.8	42
4	20	120	150	40	0.8	1.7	41.4	52.0	6.6	5.6	5.3	34
5	20	10	40	95—100	0.9	2.2	73.7	22.8	3.5	9.8	3.3	44
6	30	60	90	50	2.0	0.95	67.1	23.1	9.8	22.7	5.8	19
7	30	45	75	50—55	1.95	1.1	60.0	27.5	12.5	20.2	6.7	22
8	40	80	110	50—55	1.95	1.05	61.9	10.2	27.9	20.3	3.3	21
9	30	60	210	50—60	2.0	0.3	61.5	14.3	24.2	20.9	3.8	6
10	30	60	210	50—60	2.3	0.2	63.7	13.8	22.5	24.7	4.0	4
11	40	60	210	50—60	3.3	0.15	58.7	14.7	26.6	32.9	6.1	3
12	40	60	210	50—60	3.1	0.25	60.0	13.8	26.2	31.3	5.4	5

Found for 1 g "acid" fraction 0.3500, 0.3520 g NaOH. Calculated on the basis of the sublimation data 0.3398, 0.3448 g NaOH (in Experiments 1 and 4).

20 ml 0.1 N caustic soda and was indirectly titrated with 0.1 N hydrochloric acid in the presence of phenolphthalein. In this manner, the quantity of caustic soda consumed by 1 g of "acid" fraction was determined. These data were compared with the calculated quantity of alkali necessary for neutralization of 1 g of "acid" fraction (on the basis of the sublimation data). The data given show that the divergence between the acid numbers found for the "acid" fraction and those calculated on the basis of sublimation is not large and, consequently, the method of determining benzoic and terephthalic acids in the "acid" fraction by means of sublimation may be considered satisfactory.

SUMMARY

1. A study was made of the oxidation of cyclooctatetraene with chromic anhydride in glacial acetic acid medium. It was established that here, together with terephthalic acid and benzaldehyde, a large amount of benzoic acid is also formed.

2. The yield of terephthalic acid under various oxidation conditions was established. The attained maximum yield of the acid was 6.7%.

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THE CONDENSATION OF CYCLOHEXANONE WITH AMMONIA

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Quite recently Bradbury and coworkers [1], and, independently, Matter [2], elucidated the structure of the condensation product of 3 moles of acetone with 2 moles of NH_3 ("acetonin"), already obtained earlier by some other authors [3, 4]. They showed that the reaction of acetone with NH_3 in the presence of $CaCl_2$ and NH_4Cl yields 2, 2, 4, 4, 6-pentamethyl-2, 3, 4, 5-tetrahydropyrimidine. In studying the structure of the condensation product of acetone with NH_3 it was shown that if instead of acetone a mixture of mesityl oxide and acetone is taken, then 2, 2, 4, 4, 6-pentamethyl-2, 3, 4, 5-tetrahydropyrimidine is obtained in satisfactory yield and without the use of catalysts [1]. It was postulated that here diacetonamine is formed first, which then under reaction with acetone and NH_3 is easily transformed into the substituted tetrahydropyrimidine.

The reaction of the higher aliphatic and cyclic ketones with NH_3 has shown considerably less study. It is asserted [5] that the ketones of general formula $RCOCH_3$ (where R is an aliphatic radical with 1-8 carbon atoms), similar to acetone, can react with NH_3 with the formation of substituted tetrahydropyrimidines. The passage of a mixture of cyclohexanone and NH_3 over thorium oxide at 300-330° gave a mixture of high-boiling condensation products, the composition of which was not established, and a small amount of cyclohexylketimine [6].

We studied the reaction of cyclohexanone with NH_3 under the earlier described conditions [1, 2], in the presence of $CaCl_2$ as water-removing agent and NH_4Cl as catalyst, at room temperature, and under pressure and without pressure. A compound having the empirical formula $C_{18}H_{30}N_2$ was obtained. It could be formed from 3 moles of cyclohexanone and 2 moles of NH_3 by the reaction:

$$3C_6H_{10}O + 2NH_3 \longrightarrow C_{18}H_{30}N_2 + 3H_2O. \qquad (1)$$

The condensation product was 2, 4-dipentamethylene-5, 6-tetramethylene-2, 3, 4, 5-tetrahydropyrimidine (I). Its structure was proved via acid hydrolysis, as a result of which equimolar amounts of cyclohexanone, NH_3 and 2-(1-aminocyclohexyl)-cyclohexanone (II) were obtained. The treatment of the latter with alkali gave 2-Δ^1-cyclohexenylcyclohexanone (III):

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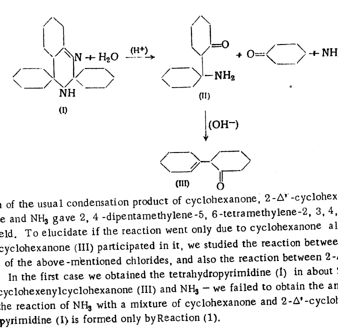

(2)

The reaction of the usual condensation product of cyclohexanone, 2-Δ'-cyclohexenylcyclohexanone (III), with with cyclohexanone and NH_3 gave 2, 4-dipentamethylene-5, 6-tetramethylene-2, 3, 4, 5-tetrahydropyrimidine (I) in about 8% yield. To elucidate if the reaction went only due to cyclohexanone alone and whether 2-Δ'-cyclohexenylcyclohexanone (III) participated in it, we studied the reaction between cyclohexanone and NH_3 in the absence of the above-mentioned chlorides, and also the reaction between 2-Δ'-cyclohexenylcyclohexanone and NH_3. In the first case we obtained the tetrahydropyrimidine (I) in about 25% yield; in the second case – from 2-Δ'-cyclohexenylcyclohexanone (III) and NH_3 – we failed to obtain the amine (II). From this we concluded that in the reaction of NH_3 with a mixture of cyclohexanone and 2-Δ'-cyclohexenylcyclohexanone (III) the tetrahydropyrimidine (I) is formed only by Reaction (1).

EXPERIMENTAL

Synthesis of 2, 4-dipentamethylene-5, 6-tetramethylene-2, 3, 4, 5-tetrahydropyrimidine (I). a) 5 moles (490 g) cyclohexanone, 40 g pulverized anhydrous $CaCl_2$ and 10 g NH_4Cl were placed in a 1-liter autoclave in which, upon cooling, was then placed 110 g (6.5 moles) NH_3. The autoclave was shaken for 48 hours. In the course of the first 2 hours a temperature increase to 35-40° was noted. The resulting solid yellowish product was ground, washed with water until removal of chlorine ions and dried in a vacuum-desiccator to constant weight. Yield 431 g (94.5%) of white powder with m. p. 52°. After precipitation with water from acetone solution and standing in the cold, white acicular crystals were obtained in poor yield, m. p. 52°; equiv. 137.5; calc. 137.

Found %: C 78.56, 78.69; H 10.98, 11.28; N 9.97, 9.69. M 280. $C_{18}H_{30}N_2$. Calculated %: C 78.85; H 10.95; N 10.20. M 274.

b) Into a mixture consisting of 203 g cyclohexanone, 60 g $CaCl_2$ and 6 g NH_4Cl was passed NH_3 at the rate of 18 liters per hour with vigorous stirring for 7 hours. After washing and drying, the yield was 130 g (70%) of (I) with the cited constants.

(I) in a dry state is very stable in air and, upon prolonged standing, turns slightly yellowish; it is readily soluble in ordinary organic solvents, insoluble in water, is hydrolyzed by dilute mineral acids even in the cold, is not hydrolyzed by alkalis, forms a light-brown, very viscous, slowly crystallizing liquid when melted which decomposes to form liquid products upon being heated in vacuum.

Hydrolysis of 2, 4-dipentamethylene-5, 6-tetramethylene-2, 3, 4, 5-tetrahydropyrimidine (I). 50 g of (I) was dissolved in 160 ml 10.9% H_2SO_4 solution. After 24 hours, the hydrolyzed solution was extracted 5 times with 25 ml portions of benzene. Using the hydroxylamine method, 13.9 g (78%) cyclohexanone was found in the benzene extract (the oxime had m. p. 88°, literature data [7] give 89-90°). A mixed sample gave no depression.

After extraction, 300 ml acetone was added to 25 ml of hydrolyzed solution. 1.6 g (100%) ammonium sulfate was precipitated out. Upon final addition of 700 ml acetone, 3.9 g (66%) 2-(1-aminocyclohexyl)-cyclohexanone sulfate came down in the form of a white powder with m. p. 108°, readily soluble in water and alcohols and insoluble in ether, benzene, acetone and in chloroform.

Found %: N 5.70, 5.75; SO_4^{2-} 19.30, 19.35; NH_2 7.35 (Van Slyke). $C_{24}H_{42}O_2N_2 \cdot H_2SO_4$. Calculated %: N 5.74; SO_4^{2-} 19.65; NH_2 6.55.

When the sulfate of 2-(1-aminocyclohexyl)-cyclohexanone was treated with an excess of concentrated caustic soda solution, a mixture was obtained which consisted of a lower aqueous and upper organic layer. The latter was distilled twice in vacuum. We obtained 2-Δ'-cyclohexenylcyclohexanone (III) with b. p. 124° (5 mm), d_4^{20} 1.002, n_D^{20} 1.5054, which is in agreement with the literature data [8].

87 g sulfate of 2-(1-aminocyclohexyl)-cyclohexanone was treated with 450 ml of 15% ammonia solution. The amine (II) which separated out was extracted with 150 ml ether, the main bulk of which was driven off on a water bath at 50°. After removal of the remaining ether in vacuum, we obtained 60 g (86.5%) of 2-(1-aminocyclohexyl)-cyclohexanone (II) in the form of viscous yellowish liquid, difficultly soluble in water and readily soluble in ordinary organic solvents, distilling with decomposition in vacuum.

d_4^{20} 1.0280, n_D^{20} 1.5058; MR_D 56.35; calc. 56.65.

Found %: C 73.60, 74.22; H 11.00, 10.94; N 7.13, 6.81. Equiv. 195.4. $C_{12}H_{21}ON$. Calculated %: C 73.85; H 10.76; N 7.18. Equiv. 195.

Reaction of 2-Δ'-cyclohexenylcyclohexanone (III) with NH_3. Into 112 g of (III), prepared by condensation of cyclohexanone in the presence of H_2SO_4 [9], NH_3 was passed at the rate of 18 liters per hour with vigorous stirring for 16 hours. 62 g of cyclohexanone was then added and passage of NH_3 was continued for 16 hours more. A small amount of alkali was added to a weighed sample of the liquid mixture obtained and all the NH_3 which evolved was removed by boiling, after which it was acidified with sulfuric acid, boiled with under reflux for 30 minutes and again alkalized. The NH_3 which then evolved was then trapped by a titrated solution of hydrochloric acid. 0.8% nitrogen was found. Upon treatment with alkali, both the dissolved NH_3 and also the NH_3 that formed during hydrolysis of the ketimino group and decomposition of amine (II) were subject to removal; therefore, the nitrogen that came off upon acid hydrolysis was the nitrogen of the tetrahydropyrimidine ring (I). The found nitrogen content corresponded to a yield of tetrahydropyrimidine (I) of about 8% of theoretical by the sum of both ketones.

NH_3 was passed at the rate of 18 liters per hour into 100 g of cyclohexanone with vigorous stirring for 16 hours. 2.7 g of the resulting liquid was placed in a vacuum desiccator. After 24 hours and removal of the unreacted cyclohexanone, coarse crystals came down. After washing with water, we obtained 0.68 g (24%) of 2, 4-dipentamethylene-5, 6-tetramethylene-2, 3, 4, 5-tetrahydropyrimidine, similar in constants to the above-described (I).

Into 100 g of 2-Δ'-cyclohexenylcyclohexanone (III) was passed NH_3 at the rate of 18 liters per hour for 16 hours with vigorous stirring. 2.7 g of the liquid obtained was placed in a vacuum-desiccator; all the ammonia was driven off, found equiv. 9360. After addition of 3 drops of water, the liquid was again placed in a vacuum-desiccator. The dried product was neutral. Evidently, the ammonia reacted with 2-Δ'-cyclohexenylcyclohexanone (III) to form only the rapidly hydrolyzed (by water) 2-Δ'-cyclohexenyl-cyclohexylketimine. 2-(1-Aminocyclohexyl)-cyclohexanone (II) was not obtained.

SUMMARY

The condensation of cyclohexanone with ammonia gave 2, 4-dipentamethylene-5, 6-tetramethylene-2, 3, 4, 5-tetrahydropyrimidine. Hydrolysis of the latter gave 2-(1-aminocyclohexyl)-cyclohexanone. Both compounds are new.

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OXIDIZABILITY OF 1,2-DIPHENYL-4-n-BUTYLPYRAZOLIDIN-3,5-DIONE

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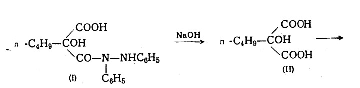
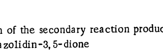
In the synthesis of 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione from n-butylmalonic ester and hydrazobenzene [1] in the presence of sodium ethylate we observed, in some of the experiments, that in addition to the main substance 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione with m.p. 104-106°, there is also formed a small amount of a secondary reaction product with m.p. 132-133°. The separation of these two substances is quite easy, since the secondary product is more soluble in alcohol; it was isolated from the mother liquor obtained in the recrystallization of the 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione. It could be assumed that the secondary product with m.p. 132-133° is the open-chain substance $COOC_2H_5-CH(n\text{-}C_4H_9)-CON(C_6H_5)-NHC_6H_5$, which was formed as the result of incomplete condensation and which could possibly be converted into 1,2-diphenyl-4-n--butylpyrazolidin-3,5-dione. However, this was not confirmed, and an explanation of the reasons for the formation of the secondary compound proved possible only after the structure of this new substance was accurately established. On the basis of its elementary analysis, the secondary substance shows 1 more oxygen atom than does 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione. In contrast to it, the secondary substance was characterized by exceeding instability and even when stirred with dilute sodium hydroxide solution in the cold it was cleaved with the formation of an acid, the sodium salt of which was poorly soluble in alkali solution and usually deposited in the precipitate. Judging from its elementary analysis, titration and properties, this acid could have the structure $COOH-CH(OC_4H_9)-CON(C_6H_5)-NHC_6H_5$. Further saponification of this compound with aqueous sodium hydroxide solution under heating led to hydrazobenzene and a dibasic acid, devoid of nitrogen, which was easily and quantitatively decarboxylated when heated at the melting point to yield a new acid with m.p. 55-60°. Titration and determination of the melting point revealed that α-hydroxycaproic acid was formed here. To conclusively prove the position of the hydroxyl group, the hydroxycaproic acid was oxidized with potassium permanganate in alkaline medium. n-Valeric acid was isolated after the oxidation, which was identified on the basis of titration, melting point of acid itself, its acid chloride, and the melting point of its amide. The valeric acid could have been formed only from α-hydroxycaproic acid (III) and in respective order from n-butyltartronic acid (II) and the monodiphenylhydrazide of n-butyltartronic acid (I):



A molecular weight determination of the secondary reaction product by the Rast method revealed that it is 1,2-diphenyl-4-n-butyl-4-hydroxypyrazolidin-3,5-dione



i.e. it is oxidized 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione. In studying the conditions for its formation we found that the oxidation of the 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione during reaction proceeds under the influence of atmospheric oxygen in the essential presence of hydrazobenzene. The oxidation with air fails to proceed in the absence of hydrazobenzene, which indicates that here hydrazobenzene functions as an oxygen carrier.

EXPERIMENTAL

1,2-Diphenyl-4-n-butylpyrazolidin-3,5-dione was prepared from hydrazobenzene and n-butylmalonic ester in anhydrous alcohol medium in the presence of sodium ethoxide [1] and was purified by recrystallization from alcohol. From the mother liquors, after recrystallization, was isolated a side product, readily soluble in alcohol, with m.p. 136-136.5°, which was not homogeneous, since only after repeated recrystallizations from 50% alcohol, did it have a constant m.p. 132-133°. The substance was insoluble in water.

Found %: C 70.47, 70.24; H 6.20, 6.12; N 9.07, 8.85. M 308 (Rast). $C_{19}H_{20}O_3N_2$. Calculated %: C 70.34; H 6.21; N 8.63. M 324.4.

Cleavage of side product. 26.2 g of side reaction product was mixed with 220 ml 8% caustic soda solution, the insoluble portion was filtered off and repeatedly mixed with 250 ml water and again filtered off. Both mother liquors were extracted separately with dichloroethane, decolorized with charcoal and after filtration, were acidified with dilute hydrochloric acid until an acid reaction was obtained on Congo. The substance which came down was filtered off and washed with water. From the first mother liquor, 3.31 g of extremely impure substance was obtained with m.p. 120-121° which was not investigated further, and from the second mother liquor was obtained 12.4 g of substance with m.p. 141.5°. The latter substance was recrystallized twice from 50% alcohol. M.p. 144-145° (with evolution of gas bubbles). The substance was almost insoluble in cold water, readily soluble in ethyl alcohol and soluble in sodium bicarbonate solution.

Found %: C 66.77, 66.48; H 6.45, 6.78; N 8.18, 8.32. M 344. $C_{19}H_{22}O_4N_2$. Calculated %: C 66.64; H 6.47; N 8.18. M 341.

The obtained substance corresponded to the mono-N,N'-diphenylhydrazide of n-butyltartronic acid (I).

Hydrolysis of the mono-N,N'-diphenylhydrazide of n-butyltartronic acid. 9.22 g of mono-diphenylhydrazide of n-butyltartronic acid was heated on a boiling water bath with 100 ml of 6% caustic soda for 2 hours with stirring. Upon cooling, the hydrazobenzene was filtered off. The mother liquor was extracted 3 times with dichloroethane, decolorized with charcoal, filtered off and acidified with dilute hydrochloric acid until an acid reaction was obtained on Congo. The acid solution was extracted 11 times with ether. The ether was driven off from the dried ethereal extract and 4.44 g of impure acid with m.p. 124-126° remained. After recrystallization from chloroform, it had m.p. 126-127° (decomp.). Yield 3.8 g (80%). The substance was soluble in water, very readily soluble in alcohol and in ether.

Found %: C 47.97, 47.63; H 6.97, 6.72. M 177. $C_7H_{12}O_5$. Calculated %: C 47.72; H 6.86. M 176.2.

The obtained substance was n-butyltartronic acid (II).

Decarboxylation of n-butyltartronic acid. 5 g of the above-obtained acid was heated at 125-130° until cessation of the evolution of carbon dioxide gas which was absorbed by a solution of barium hydroxide. 1.2 g carbon dioxide gas evolved. The new acid which formed melted at 57-60° and had an odor similar to that of caproic acid. The substance was soluble in water, alcohol and in ether Found M 140. $C_6H_{12}O_3$. Calculated M 132, i.e. by analysis and properties it was α-hydroxycaproic acid (III).

Oxidation of α-hydroxycaproic acid. A saturated solution of potassium permanganate was gradually added with stirring at room temperature to 7 g of hydroxycaproic acid, 3 g of soda in 30 ml water until disappearance of pink coloration. The next day the manganese dioxide was filtered off, washed two times with hot water and the wash water was combined with the main filtrate. The filtrate was steamed down in an open cup to a volume of 20 ml and was acidified with dilute sulfuric acid under a layer of ether until an acid reaction was obtained on Congo. The sulfate salts that came down were filtered off, washed with ether, the ethereal extract was separated off and the aqueous solution was extracted two more times with ether. The combined ethereal extracts were dried with anhydrous sodium sulfate, the ether was driven off and the remaining substance was distilled. The following fractions were obtained: 1st with b.p. 130-179°, 0.77 g; 2nd with b.p. 179-186°, 1.7 g (the literature data for n-valeric acid give b.p. 186° [2]).

Investigation of 2nd fraction. Found M 101.8. $C_5H_{10}O_2$. Calculated M 102.13.

1.08 g of the 2nd fraction, b.p. 179-186°, and 1.5 g of thionyl chloride were heated for 25 minutes at 80° with periodic stirring. The mixture was then distilled two times. An acid chloride with b.p. 123-128.5 was obtained, 0.57 g (b.p. 127.2° [3] is given for valeryl chloride).

0.57 g of the obtained acid chloride was gradually added to 4 ml of cooled (with ice water) ammonia solution (d 0.905). The precipitate which came down was filtered off. After recrystallization from ethyl acetate, it had m.p. 103-104.5° (the literature data [4] give for the amide of n-valeric acid m.p. 106°).

Oxidation of 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione with atmospheric oxygen. 10 g of 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione was added to a solution of sodium ethoxide, prepared from 0.75 g metallic sodium and 100 ml alcohol and the alcohol was slowly driven off in the course of 5 hours while air was simultaneously passed through the reaction mixture. The residue was dissolved in water, extracted with dichloroethane, decolorized with charcoal, filtered, and the solution was neutralized with dilute hydrochloric acid. The substance which came down was recrystallized from alcohol. 8.48 g of starting compound with m.p. 106° was returned. After concentration, 0.29 g more of starting compound with m.p. 101-103° was obtained from the mother liquor. The oxidation product of 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione was not found under these conditions.

Oxidation of 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione with atmospheric oxygen in the presence of hydrazobenzene. The experiment was carried out under the same conditions except in the presence of 6 g hydrazobenzene. After recrystallization from alcohol, 6.1 g of starting substance with m.p. 105° was obtained and from the alcoholic mother liquor, after recrystallization, 1.15 g of oxidation product 1,2-diphenyl-4-n-butyl-4-hydroxypyrazolidin-3,5-dione was isolated. For cleavage of the pyrazolidine ring the substance was mixed with dilute caustic soda solution, the sodium salt which came down was dissolved in water and from the dilute hydrochloric acid solution was precipitated the mono-diphenylhydrazide of n-butyltartronic acid which was purified by recrystallization from 50% alcohol. It melted at 144° and gave no depression with the mono-diphenylhydrazide of n-butyltartronic acid which was obtained previously. Consequently, in the presence of hydrazobenzene the oxidation of 1,2-diphenyl-4-n-butylpyrazolidin-3,5-dione with atmospheric oxygen to the hydroxy derivative took place.

SUMMARY

1. The structure of the secondary product, formed in the condensation of n-butylmalonic ester with hydrazobenzene in a medium of alcoholic sodium ethylate solution, was determined, which proved to be 1,2-diphenyl-4-n-butyl-4-hydroxypyrazolidin-3,5-dione.

2. It was elucidated that the formation of this secondary reaction product proceeds under oxidation with atmospheric oxygen in the essential presence of hydrazobenzene.

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PREPARATION OF α-NAPHTHYLNITROMETHANE AND ITS DERIVATIVES

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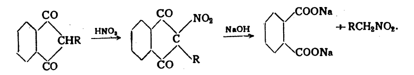
α-Naphthylnitromethane is a difficultly available compound, and only a single study has been devoted to its synthesis, where it was obtained by the reaction of α-naphthylacetonitrile with ethyl nitrate in the presence of sodium ethylate.

Wislicenus and Wren [1], who realized this synthesis 50 years ago, failed to communicate the yield of either the intermediate products or of the final nitro compound.

Up to now the attempts to obtain α-naphthylnitromethane by the direct nitration of α-methylnaphthalene with nitric acid have been unsuccessful. Treatment with anhydrous nitric acid gives the 4-nitro derivative and a mixture of difficultly separable oily products of unknown structure [2]; if acid (d 1.36) containing nitrogen oxides is used, then the 4-nitro derivative is obtained as the solitary product [3]. In general, the derivatives of α-naphthylnitromethane with substituents in the ring are unknown.

Earlier, one of us [4] had developed a general method for the preparation of compounds with the nitromethyl group, which can be depicted by the scheme:

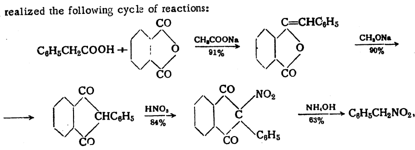


The 1,3-indandione derivatives on which this synthesis is based are readily available substances. This is especially true of the diketones with heterocyclic and aryl substituents in the two position. The first are the phthalones, being obtained in nearly quantitative yield by the fusion of phthalic anhydride and a heterocyclic compound with a sufficiently active methyl group [5].

In the case of aryl derivatives of the indandione good results are obtained if the phthalides are synthesized from arylacetic acids and phthalic anhydride, with their subsequent isomerization into diketones under the influence of alcoholic sodium alcoholates.

The preparation of arylnitromethanes had been studied by one of us earlier on the example of phenylacetic acid [6].

Having realized the following cycle of reactions:



in the final end we obtained phenylnitromethane in 43% yield, based on starting phenylacetic acid.

As is known, the nuclear substituted derivatives of α-naphthylacetic acid have become readily available substances, and α-naphthylacetic acid itself is obtained on a commercial scale in good yields. The method for the preparation of these compounds is based on the reaction of chloroacetic acid with naphthalene and its derivatives [7, 8].

Using the above cycle of reactions based on the example of phenylacetic acid, we obtained α-naphthylnitromethane, for which the whole synthesis is given in the EXPERIMENTAL. Based on the starting naphthylacetic acid the yield is 20-30%.

To obtain 4-nitro- α-naphthylnitromethane we used the method previously described by us and used at the time for the synthesis of 4-nitrophenylnitromethane [9].

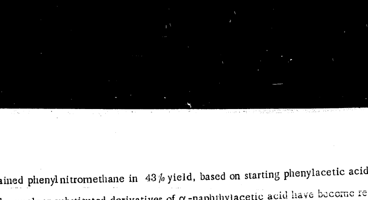
It consisted in the nitration of benzylidenephthalide

with subsequent isomerization into the diketone and then by the scheme given above. It was found that the aryl residue in phthalides is extremely reactive and benzylidenephthalide in its character is reminiscent of toluene.

The nitration of α-naphthylidenephthalide also gave the nitro derivative. After the nitrophthalide was isomerized into the diketone, nitration and hydrolysis of the nitro diketone gave in good yield the corresponding nitro compound – 4-nitro-α-naphthylnitromethane.

The position of the nitro group was shown in two ways. On the one hand, by the oxidation of the nitrophthalide at the ethylene bond, and on the other, by treatment of the final derivative containing a nitromethyl group with sulfuric acid. 4-Nitro-α-naphthoic acid was obtained in both cases. This shows that the nitro group is found in the four position.

We obtained the diketone, needed for the synthesis of 4-bromo-α-naphthylnitromethane, by the following scheme:



The position of the bromine was also shown by oxidation of the phthalide, which led to 4-bromo-α--naphthoic acid.

The whole synthesis of 4-bromo-α-naphthylnitromethane was run in the same manner as for the α--naphthylnitromethane and 4-nitro-α-naphthylnitromethane. This synthesis can be found in the EXPERIMENTAL.

EXPERIMENTAL

1. Preparation of α-naphtyl-1,3-indandione. a) 81 g α-naphthylacetic acid, 81 g phthalic anhydride and 2.5 g of anhydrous sodium acetate [10] were mixed and carefully ground in a mortar, the mixture was placed in a liter flask connected to a slanted tube for driving off the water formed during the reaction. The reaction mass was carefully heated on a gas burner until the appearance of crystals in the brown liquid melt, which usually takes about 2 hours. After cooling, the solidified mass was boiled with alcohol until a yellow powder formed. The yield of commercial product suitable for further operations was 90.5 g (76%). After recrystallization from glacial acetic acid, the substance gave fine yellow prisms with m.p. 177-178°.

Found %: C 84.29; H 4.94. $C_{19}H_{12}O_2$. Calculated %: C 83.82; H 4.41.

b) Isomerization of phthalide to 2-(α-naphthyl)-1,3-indandione was carried out according to Nathanson [11]. Boiling of 40 g phthalide in sodium methoxide (275 ml methanol and 6 g sodium) for 30 minutes with subsequent aqueous dilution and acidification yielded 35 g of rather pure diketone. The yield of unrecrystallized product was 88%. After recrystallization from acetic acid, from 20 g crude product was obtained 13.5 g of crystals in the form of thin light yellow flakes. M. p. 205-206°.

Found %: C 83.99; H 4.70. $C_{19}H_{12}O_2$. Calculated %: C 83.82; H 4.41.

2. Nitration of 2-(α-naphthyl)-1,3-indandione. 3.25 g of diketone was dissolved in 70 ml glacial acetic acid with heating and to this solution was added a nitrating mixture of 4 ml nitric acid (spec. grav. 1.52) and 8 ml glacial acetic acid. Upon cooling, 2-nitro-2-(α-naphthyl)-1,3-indandione came down. Yield 2.15 g (57%). M.p. 156°.

Found %: C 71.85; H 3.28; N 4.42. $C_{19}H_{11}O_4N$. Calculated %: C 71.95; H 3.38; N 4.41.

In the cited case the most typical yield was given. In general, it varied in the range 52-60% and in one case even reached 77%. Nitric acid (spec. grav. 1.38) can be also used with similar success.

3. Preparation of α-naphthylnitromethane. 10.3 g 2-nitro-2-(α-naphthyl)-1,3-indandione was dissolved in 300 ml 5% aqueous solution of caustic soda, employing a mechanical stirrer. Solution was continued for about 6 hours, after which the alkaline solution was filtered off and acidified with dilute acetic acid. The precipitate had the consistency of a slurry and after standing overnight, completely solidified into a brown crystalline powder.

After washing with water and drying at room temperature, 5.2 g of relatively pure α-naphthylnitromethane was obtained.

Found %: N 8.01. $C_{11}H_9O_2N$. Calculated %: N 7.49.

After recrystallization from glacial acetic acid, 3.4 g of yellow flakes with m.p. 71-72° was obtained which corresponds to the literature data for α-naphthylnitromethane.

Found %: C 70.46; H 4.59; N 7.73. $C_{11}H_9O_2N$. Calculated %: C 70.60; H 4.81; N 7.49.

4. Nitration of α-naphthylidenephthalide. 15 g of α-naphthylidenephthalide was covered with a mixture of 50 ml glacial acetic acid and 90 ml of nitric (spec. grav. 1.34) acid. The suspension was heated on a water bath to 40-45° for 5 minutes, after which the yellow crystalline powder was separated off and dried. Weight 15.2 g. M.p. about 230°.

Found %: N 5.13. $C_{19}H_{11}O_4N$. Calculated %: N 4.41.

From the analytical data it was evident that the substance contained more highly nitrated products. For purification it was boiled with benzene and the insoluble portion was filtered off. The weight of yellow needles was 9.8 g. M.p. 247°. Besides this, the benzene filtrate gave 2.8 g of substance with m.p. 253°, which amounted to 12.6 g nitro derivative or 72%, based on the starting α-naphthylidenephthalide.

Found %: N 4.50. $C_{19}H_{11}O_4N$. Calculated %: N 4.41.

After several recrystallizations, the substance had m.p. 257°; however, the product with m.p. 247-253° gave the same yield of diketone as the completely pure product.

The substance was readily soluble in hot benzene from which it could be recrystallized; it was difficultly soluble in alcohol and in benzene.

5. Preparation of 2-(4-nitro-α-naphthyl)-1,3-indandione. Isomerization was carried out by approximately the same method as was used for the α-naphthyl derivative. 5 g of nitrophthalide was covered with 25 ml 3% sodium methoxide and to the dark-violet solution was added 12 ml methanol; the mixture was boiled on a water bath for 30 minutes, after which it was poured into water. The blood-red solution was filtered and acidified with dilute hydrochloric acid. In all, 4.65 g commercial product was obtained, which after recrystallization from glacial acetic acid, yielded 3.52 g (70%) of greyish flakes with m.p. 203-204°.

Found %: N 4.48. $C_{19}H_{11}O_4N$. Calculated %: N 4.41.

6. Preparation of 2-nitro-2-(4-nitro-α-naphthyl)-1,3-indandione. 19 g of (4-nitro-α-naphthyl)-1,3-indandione was covered with 220 ml of glacial acetic acid, the mixture was heated to 45° and 220 ml of nitric acid (spec. grav. 1.34) was run in; the mixture was then shaken and carefully heated again until brown oxides of nitrogen started to evolve. After cooling with running water, the crystalline precipitate was suction-filtered off, washed with alcohol. Recrystallization from acetic acid gave 16 g of nitro derivative. M. p. 165-166°. Yield 74%.

Found %: C 62.70; H 2.54; N 7.76. $C_{19}H_{10}O_6N_2$. Calculated %: C 62.98; H 2.76; N 7.73.

7. Preparation of (4-nitro-α-naphthyl)-nitromethane. 11 g of the nitro derivative, obtained as previously described, was carefully rubbed in a mortar and covered with 200 ml of 5% aqueous solution of caustic soda and set aside at room temperature with mechanical stirring for 6 hours. The transparent solution was filtered free of insoluble substance. The weight of the latter was 0.4 g. After acidification with dilute acetic acid, a yellow precipitate in the form of fine needles came down from the filtrate. Weight 5.75 g, m.p. about 112°. After recrystallization from alcohol, 4.5 g (66%) of crystals of the nitro derivative was obtained with m.p. 116-117°.

Found %: C 56.63; H 3.30; N 12.07. $C_{11}H_8O_4N_2$. Calculated %: C 56.90; H 3.45; N 12.07.

8. Preparation of 4-nitro-α-naphthoic acid. a) From (4-nitro-α-naphthyl)-nitromethane. 0.5 g of (4-nitro-α-naphthyl)-nitromethane was covered with 5 ml 80% sulfuric acid and was carefully heated for 30 minutes on an air bath with continuous stirring. The reaction mixture was quite dark. After cooling, the mixture was diluted with water, the precipitate was separated and washed with water and then treated with sodium bicarbonate. Upon acidification, fine crystals came down with m.p. 216°. They were recrystallized from dilute alcohol. Brown needles were obtained with m.p. 219-220°.

Found %: C 60.60; H 3.28; N 6.50. $C_{11}H_7O_4N$. Calculated %: C 60.82; H 3.22; N 6.45.

The analytical data correspond to the literature data for 4-nitro-α-naphthoic acid.

b) From nitrophthalide. 2.3 g of 4-nitro-α-naphthylidenephthalide was carefully stirred with 4.5 g of sodium bichromate, the mixture was covered with 60 ml glacial acetic acid and then, carefully with vigorous shaking 5 ml concentrated sulfuric acid was added. The mixture was heated with mixing until the liquid was colored green. The hot solution was filtered and the filtrate was diluted with water. The light-yellow precipitate was separated off, washed with water and then with a saturated solution of sodium bicarbonate. The soda filtrate was acidified with dilute hydrochloric acid. After recrystallization from dilute alcohol, the light-yellow precipitate weighed 0.4 g and had m.p. 218°. The yield of acid was 25%.

Found %: N 6.58. $C_{11}H_7O_4N$. Calculated %: N 6.45.

A second recrystallization gave a substance with m.p. 219-220°.

9. Bromination of α-naphthylidenephthalide. 60 g of α-naphthylidenephthalide was covered with 450 ml of carbon tetrachloride, the suspension was heated to the boil on a water bath and then a solution of 24 ml bromine in 35 ml of the same solvent was added in small portions in the course of 45 minutes. After hydrogen bromide fumes started to evolve, the mixture was boiled in a flask with reflux condenser for 18 hours, cooled, the precipitate was separated off, washed with carbon tetrachloride and dried. The weight of the tribromo derivative was 65 g (58%). M.p. about 200°. Similar to dibromobenzylidenephthalide, the substance did not have a sharp melting point and decomposes with heating.

Found %: Br 47.08. $C_{19}H_{11}O_2Br_3$. Calculated %: Br 46.97.

10. Preparation of 4-bromo-α-naphthylidenephthalide. 65 g of substance, prepared as in the preceding, was stirred with 100 g of zinc dust and covered with 600 ml glacial acetic acid. After boiling for one hour, the mixture was decanted. Upon cooling, the solution gave a yellow crystalline powder which was separated off. The mother liquor was mixed with the remaining zinc dust and was again boiled to extract the substance remaining in mixture with the zinc dust. The filtrate gave a second portion of crystals which were combined with the first portion. Yield

24.5 g (55%) of the monobromo derivative. M.p. 203-207°. After recrystallization from acetic acid or from benzene, the substance had m.p. 223-224°; however, for all subsequent work, the product with m.p. 203-207° was used which gave practically the same yields of diketone as the completely pure product.

Found %: Br 22.46. $C_{19}H_{11}O_2Br$. Calculated %: Br 22.79.

The position of the bromine atom in the naphthalene ring was established in the following manner. 5 g of the monobromo derivative was oxidized with sodium bichromate by the method described in Preparation 8. After acidification of the solution of the acid in bicarbonate, the precipitate which came down was recrystallized from glacial acetic acid. The yellow needles of 4-bromo-α-naphthoic acid melted at 218-219° (literature data give 217-220°).

Found %: Br 31.83, 31.20. $C_{11}H_7O_2Br$. Calculated %: Br 31.47.

11. Preparation of the diketone. Isomerization of the phthalide to the diketone was carried out by the above described method as for other phthalides. From 15 g of phthalide was obtained 14.5 g of crude diketone with m.p. 198-200°. After recrystallization from alcohol, they were in the form of oblong flakes with m.p. 207-208°.

Found %: Br 22.98. $C_{19}H_{11}O_2Br$. Calculated %: Br 22.79.

12. Nitration of the diketone. 9.5 g of (4-bromo-α-naphthyl)-1,3-indandione was covered with 150 ml glacial acetic acid and heated mildly. Upon shaking, 60 ml of a mixture of equal volumes of glacial and nitric (spec. grav. 1.48) acids was added to the suspension. The suspension was heated to 50-55° and held at this temperature for 15 minutes and then cooled. The precipitate which came down was separated off and washed with alcohol. Yield 7.1 g of crude nitration product with m.p. 147-148°. Impurities were extracted by boiling with acetic acid. The insoluble diketone had m.p. 160-161°. Recrystallization from acetic acid did not change the melting point. Yield 4.85 g (45%).

Found %: N 3.54; Br 19.86. $C_{19}H_{10}O_4NBr$. Calculated %: N 3.53; Br 20.20.

13. Preparation of (4-bromo-α-naphthyl)-nitromethane. 3.7 g of the nitrodiketone was covered with 30 ml of 10% caustic soda and the mixture was mechanically stirred at room temperature for 7 hours, diluted with water and filtered. 0.65 g of substance with m.p. 160-161° remained undissolved. The filtrate was acidified with dilute acetic acid until a slight turbidity appeared and was set aside for 12 hours. The residue of (4-bromo-α-naphthyl)-nitromethane weighed 1.85 g, with m.p. 85-86°. The yield of crude product was 90%. After recrystallization from alcohol, 0.9 g of nitro derivative was obtained with m.p. 91-92°.

Found %: N 5.31; Br 29.50, 29.67. $C_{11}H_8O_2NBr$. Calculated %: N 5.26; Br 30.07.

SUMMARY

A method was developed for the synthesis of α-naphthylnitromethane and some of its derivatives.

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PYRIDO-(3,4-d)-THIAZOLE DERIVATIVES

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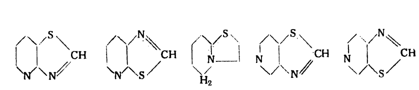
The condensed system of thiazole with pyridine, known as the pyridothiazole nucleus, has been studied but slightly. Of the five possible pyridothiazole isomers

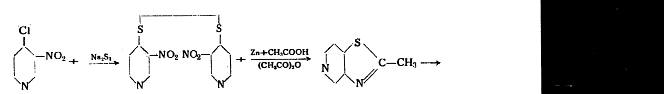


(2,3-d) (3,2-d) 5H-(2,1-b) (3,4-d) (4,3-d)

only the first three derivatives are known, and the number of their known individual representatives are extremely few. The first derivatives of pyrido-(2,3-d)-thiazole and pyrido-(3,2-d)-thiazole were synthesized by the Japanese chemists [1], but the unsubstituted pyridothiazoles themselves have not been obtained up to now.

The purpose of the present study was to synthesize the new pyrido-(3,4-d)-thiazole and some of its derivatives: the 2-carboxylic acid, its amide, the hydrazide and some hydrazones, in order to elucidate the activity of the indicated compounds on the tubercle bacillus.

We realized the synthesis in the following manner: the heating of 3-nitro-4-chloropyridine with sodium disulfide gave the disulfide (I), the reduction of which with zinc dust in acetic acid gave 3-amino-4-mercaptopyridine, not isolated from the reaction mixture, and when boiled with acetic anhydride the latter was cyclized to 2-methylpyrido-(3,4-d)-thiazole (II). Oxidation of (II) with potassium permanganate gave pyrido-(3,4-d)-thiazole-2-carboxylic acid (III), and the acid in turn was converted into the ester (IV); from the latter were obtained the amide (V) and hydrazide (VI), and from the hydrazide the two hydrazones with benzaldehyde and salicylaldehyde. The indicated transformations are depicted by the following scheme:



(I) (II)

(scheme continued on following page)

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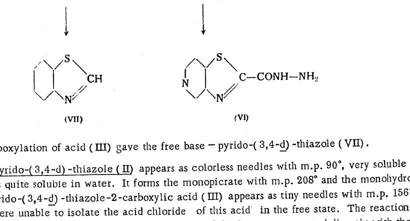

The decarboxylation of acid (III) gave the free base – pyrido-(3,4-d)-thiazole (VII).

2-Methylpyrido-(3,4-d)-thiazole (II) appears as colorless needles with m.p. 90°, very soluble in most organic solvents and quite soluble in water. It forms the monopicrate with m.p. 208° and the monohydrochloride with m.p. 238°. Pyrido-(3,4-d)-thiazole-2-carboxylic acid (III) appears as tiny needles with m.p. 156° (decomp.). We were unable to isolate the acid chloride of this acid in the free state. The reaction product of the acid with thionyl chloride, after removal of the excess of the latter, was reacted directly with the alcohol. The methyl ester (IV) has m.p. 71°. The amide (V) is obtained from the ester (IV) without any difficulty, but the hydrazide (VI) of this acid is obtained only at a temperature not exceeding 30°, probably, due to the fact that when heated with hydrazine hydrate the pyridothiazole ring is ruptured. The formation of acylhydrazones from the hydrazide is both easy and quatitative.

EXPERIMENTAL

4-Chloro-3-nitropyridine, necessary for the described synthesis, is known. The starting product for its preparation is pyridine, which via pyridylpyridinium dichloride is converted to 4-hydroxypyridine [2], and then, with nitration, into 3-nitro-4-hydroxypyridine [3]. Replacement of the hydroxy group with chlorine to prepare 4-chloro-3-nitropyridine was carried out under the conditions described by Bremer [3].

3,3'-Dinitro-4,4'-dipyridyl disulfide (I). 48 g of crystalline sodium sulfide was dissolved in 100 ml of boiling alcohol, 6.4 g of sulfur was then added and the mixture was boiled for 10 minutes. Upon cooling, 39 g 3-nitro-4-chloropyridine was added in small portions with shaking to the above mixture. At first the solution darkened, then a crystalline precipitate coated the walls of the flask and finally, a viscous light-yellow mass formed. After this, the mixture was heated for 10 minutes on a water bath at 70-80°; on cooling, the precipitate was filtered off, suspended in 100 ml of water, set aside for 30 minutes and again filtered off; after drying, it was recrystallized from glacial acetic acid. Yield 19.6 g (62%). Light-yellow needles with m.p. 216°.

2-Methylpyrido-(3,4-d)-thiazole (II). A well rubbed mixture of 19.6 g disulfide (I) and 60 g zinc dust, previously treated with dilute hydrochloric acid [4], was added in small portions with mechanical stirring in the course of one and a half hours to 150 ml of boiling acetic acid. The mixture was then boiled with mixing for one hour more, 40 ml acetic anhydride was added and boiling with mixing was continued for 3 hours more. On cooling, the mixture was alkalized with a large excess of 40% caustic soda solution, and Compound (II) was extracted repeatedly with chloroform (test for completeness of extraction). After this was driven off, a colored crystalline precipitate remained with an odor similar to that of acetamide. It was again dissolved in chloroform and passed through a layer of aluminum oxide 15 cm high. After evaporation of the solvent, the precipitate was recrystallized from a small quantity of ligroine. Yield 12.7 g (67%). M.p. 90°.

Found %: N 18.20, 18.28; S 21.21, 21.02. $C_7H_6N_2S$. Calculated %: N 18.66; S 21.33.

The picrate was obtained from alcoholic solution. It was recrystallized from alcohol, m.p. 208°.

Found %: N 18.28, 28.38; S 8.42, 8.60. $C_{13}H_9O_7N_5S$ Calculated %: N 18.47; S 8.44.

The hydrochloride salt was prepared by addition of an ethereal solution of hydrogen chloride to an ethereal solution of 2-methylpyrido-(3,4-d)-thiazole. The white precipitate which came down was recrystallized from alcohol with ether. M.p. 238°.

Found %: N 15.20, 14.96. $C_7H_7N_2ClS$. Calculated %: N 15.01.

Pyrido-(3,4-d)-thiazole-2-carboxylic acid (III). 9 g of rubbed potassium permanganate and 12 g of Compound (II) were added to 150 ml water with mixing and heating on a water bath. The mixture was mixed for 30 minutes and 150 ml water and 9 g potassium permanganate were again added and the mixture was again heated with mixing until the permanganate color disappeared. The hot solution was filtered and the precipitate was extracted 2 times with hot water. The combined filtrates were steamed down to 20-25 ml volume and upon cooling, dilute hydrochloric acid was carefully added until there was a weakly acid reaction; a white precipitate came down which was set aside for 1 hour and then purified by reprecipitation with hydrochloric acid from solution in soda. The yield of pyrido-(3,4-d)-thiazole-2-carboxylic acid (III), washed with a small quantity of water and dried in a vacuum-desiccator over sulfuric acid, was 2.8 g. M. p. 156° (decomp.). After alkalization with sodium carbonate, 4.5 g of unreacted 2-methylpyridothiazole with m.p. 90° came down from the filtrate. Thus a total of 7.5 g 2-methylpyridothiazole reacted. Yield of acid onreacted thiazole was 36%.

Found %: N 15.45, 15.64; S 17.89, 18.00. $C_7H_4O_2N_2S$. Calculated %: N 15.55; S 17.77.

Methyl ester of pyrido-(3,4-d)-thiazole-2-carboxylic acid (IV). 2 g of acid (III) was mixed with 10 ml thionyl chloride and the mixture was heated on a water bath to the boil for 3 hours. The excess of thionyl chloride was then driven off in the vacuum of a water-jet pump and 20 ml anhydrous methyl alcohol was added to the residue; the mixture was boiled for one hour more. The alcohol was driven off and 15 ml of saturated sodium carbonate solution was added to the residue. The methyl ester of pyrido-(3,4-d)-thiazole-2-carboxylic acid was repeatedly extracted with chloroform. After driving off the chloroform, the residue was recrystallized from ligroine. M.p. 171°. Yield 1.2 g (56%). It gave no depression in a test mixture with the methyl ester obtained from acid (III) and diazomethane.

Found %: N 14.24, 14.29. $C_8H_6O_2N_2S$. Calculated %: N 14.43.

Amide of pyrido-(3,4-d)-thiazole-2-carboxylic acid (V). To 0.45 g of ester (IV) was added 10 ml of concentrated aqueous ammonia solution and the mixture was set aside for 48 hours. The precipitate was filtered off, washed with water and recrystallized from water. Yield 0.3 g (71%). Colorless needles with m.p. 262°.

Found %: N 23.53, 23.58. $C_7H_5ON_3S$. Calculated %: N 23.46.

Hydrazide of pyrido-(3,4-d)-thiazole-2-carboxylic acid (VI). To a solution of 0.3 g of ester (IV) in 10 ml methyl alcohol was added 0.3 g hydrazine hydrate at room temperature. After 3-5 minutes, a precipitate came down from solution in the form of white needles. It was filtered off and recrystallized from alcohol. Yield of pure product (VI) 0.25 g (83%). Light-yellow needles with m.p. 232°.

Found %: N 28.40, 28.22. $C_7H_6ON_4S$. Calculated %: N 28.86.

If the reaction of hydrazine hydrate with ester (IV) is carried out with heating, then hydrazide (VI) does not form, due probably to the fact that hydrazine hydrate cleaves the thiazole nucleus. The fact that we did not succeed in preparing the analytically pure substance was probably due to the partial cleavage of the thiazole ring even at room temperature.

Hydrazone with benzaldehyde. To a solution of 0.2 g of the hydrazide of pyrido-(3,4-d)-thiazole-2-carboxylic acid (VI) in 3 ml glacial acetic acid (heated to the boil) was added a solution of 0.2 g benzaldehyde in 1 ml glacial acetic acid and the mixture was boiled for 5 minutes. On cooling, 2 ml water was added to the mixture and the precipitate which came down was recrystallized from alcohol. Colorless needles with m.p. 241°.

Found %: N 19.49, 19.50. $C_{14}H_{10}ON_4S$. Calculated %: N 19.53.

The hydrazone with salicylaldehyde was prepared in the same manner as above. M.p. 290°.

Found %: N 17.82. $C_{14}H_{10}O_2N_4S \cdot H_2O$. Calculated %: N 17.72.

Pyrido-(3,4-d)-thiazole (VII). 1 g of acid (III) was heated in a test tube on an oil bath at 175-180° for 10 minutes and the residue was then extracted with boiling ligroine, the solution was decolorized with charcoal and after the solvent was driven off, the residue was again dissolved in a small quantity of petroleum ether, filtered and the ether was steamed off. The residue was in the form of colorless needles with m.p. 105°. Yield 0.4 g (53%).

Found %: N 17.82. $C_{14}H_{10}O_2N_4S \cdot H_2O$. Calculated %: N 17.72.

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SUMMARY

1. We prepared 2-methylpyrido-(3,4-d)-thiazole, pyrido-(3,4-d)-thiazole-2-carboxylic acid, its methyl ester, the amide, hydrazide and two hydrazones.

2. The decarboxylation of pyrido-(3,4-d)-thiazole-2-carboxylic acid gave pyrido-(3,4-d)-thiazole.

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TABLE OF CONTENTS

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TABLE OF CONTENTS (continued)

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TABLE OF CONTENTS (continued)

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TABLE OF CONTENTS (continued)

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